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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/823,630	04/14/2004	Michel Armand	213411.00032	4612

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EXAMINER

CHOI, LING SIU

ART UNIT PAPER NUMBER

1713

DATE MAILED: 10/10/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

*2*

<b>Office Action Summary</b>	<b>Application No.</b> 10/823,630	<b>Applicant(s)</b> ARMAND ET AL.	
	<b>Examiner</b> Ling-Siu Choi	<b>Art Unit</b> 1713	

**-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --**

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
  - If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
  - Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133).
- Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

- 1) ☒ Responsive to communication(s) filed on 14 April 2004.
- 2a) ☐ This action is **FINAL**.                      2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

- 4) ☒ Claim(s) 1-16 is/are pending in the application.
- 4a) Of the above claim(s) 5-16 is/are withdrawn from consideration.
- 5) ☐ Claim(s) \_\_\_\_\_ is/are allowed.
- 6) ☒ Claim(s) 1-4 is/are rejected.
- 7) ☐ Claim(s) \_\_\_\_\_ is/are objected to.
- 8) ☐ Claim(s) \_\_\_\_\_ are subject to restriction and/or election requirement.

**Application Papers**

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on \_\_\_\_\_ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.  
     Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).  
     Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**Priority under 35 U.S.C. § 119**

- 12) ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☒ All    b) ☐ Some \*    c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☒ Certified copies of the priority documents have been received in Application No. 09/361,962.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

\* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

- |  |   |
|--|---|
| 1) <input checked="" type="checkbox"/> Notice of References Cited (PTO-892)                                | 4) <input type="checkbox"/> Interview Summary (PTO-413)<br>Paper No(s)/Mail Date. _____ |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948)                       | 5) <input type="checkbox"/> Notice of Informal Patent Application                       |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO/SB/08)<br>Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____  |

### DETAILED ACTION

1. This Office Action is in response to the Response to Restriction Requirement filed July 25, 2006. Claims 1-4 of Group 1 have been elected with traverse. Applicants alleged that "all of the pending claims have the common characteristic of the compounds of formula I.....Accordingly, there appears to be no reason to divide these claims into three different applications." It is noted that the compounds of formula I represents a huge number of compounds ranging from polymers to organic compounds and having different properties and part of compounds represented by the Formula I are not novel. Thus, the patentability of each group does not depend on the compounds of formula I and depend on the combination of the compounds of Formula I and other limitation(s). In conclusion, the restriction is proper and is made as final.

### ***Double Patenting***

2. The nonstatutory double patenting rejection is based on a judicially created doctrine grounded in public policy (a policy reflected in the statute) so as to prevent the unjustified or improper timewise extension of the "right to exclude" granted by a patent and to prevent possible harassment by multiple assignees. See *In re Goodman*, 11 F.3d 1046, 29 USPQ2d 2010 (Fed. Cir. 1993); *In re Longi*, 759 F.2d 887, 225 USPQ 645 (Fed. Cir. 1985); *In re Van Ornum*, 686 F.2d 937, 214 USPQ 761 (CCPA 1982); *In re Vogel*, 422 F.2d 438, 164 USPQ 619 (CCPA 1970); and, *In re Thorington*, 418 F.2d 528, 163 USPQ 644 (CCPA 1969).

A timely filed terminal disclaimer in compliance with 37 CFR 1.321(c) may be used to overcome an actual or provisional rejection based on a nonstatutory double patenting ground provided the conflicting application or patent is shown to be commonly owned with this application. See 37 CFR 1.130(b).

Effective January 1, 1994, a registered attorney or agent of record may sign a terminal disclaimer. A terminal disclaimer signed by the assignee must fully comply with

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37 CFR 3.73(b).

3. Claim 2 is rejected on the ground of nonstatutory double patenting over claim 1 of U. S. Patent No. 6,743,877 B1 since the claims, if allowed, would improperly extend the "right to exclude" already granted in the patent.

The subject matter claimed in the instant application is fully disclosed in the patent and is covered by the patent since the patent and the application are claiming common subject matter, as follows: claim 2 of the present application encompasses claim 1 of US 6,743,877 B1.

Furthermore, there is no apparent reason why applicant was prevented from presenting claims corresponding to those of the instant application during prosecution of the application which matured into a patent. See *In re Schneller*, 397 F.2d 350, 158 USPQ 210 (CCPA 1968). See also MPEP § 804.

### ***Claim Objections***

4. Claim 1-2 and 17 is objected to because of the following informalities: (a) **Claim 1**, line 12, "then X" is suggested to be changed to --X--; (b) **Claim 1**, line 15, "substituents oxa, azaor thia; and wherein 2 R<sup>6</sup> groups" is suggested to be changed to -- substituents: oxa, azaor thia; and wherein two R<sup>6</sup> groups--; (c) **Claim 1**, line 19, "0 et p" is suggested to be changed to --0 and p--; (d) **Claim 2**, line 1, "characterised in that it is" is suggested to be changed to --wherein the compound is--; (e) **Claim 2**, line 32, "2R<sup>5</sup>" is suggested to be changed to

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--two R<sup>5</sup>--; (f) **Claim 2**, line 34, "CR<sup>5</sup>;" is suggested to be changed to --CR<sup>5</sup>; or--; (g) **Claim 4**, line 1, "characterized in they are" is suggested to be changed to --wherein the compounds are--; and (h) **Claim 4**, line 5, "2 et 3 V" is suggested to be changed to --2 and 3.7 V--.

Appropriate correction is required.

### ***Claim Rejections - 35 USC § 112***

**5. The following is a quotation of the second paragraph of 35 U.S.C. 112:**

**The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.**

6. Claims 1-4 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

**Claim 1**, line 3, "2pM<sup>+</sup>" causes indefiniteness because in order to have neutral compound, the total negative charge should be equal to the total positive charge. Thus, 2p should be replaced by nq.

**Claim 1**, lines 5-6, "M<sup>+</sup>" causes indefiniteness because it represents alkaline-earth cation, a transition metal cation, a rare earth cation, or an organometallic cation, which may not have +1 charge.

**Claim 1**, lines 6-7, the recitation "an organic cation of the "nium" type" causes indefiniteness because the Applicants do not clearly set forth the metes and bounds of the patent protection desired.

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**Claim 1**, line 19, the recitation "q varies between 0 and p" causes indefiniteness because if q is zero, Z is absent from the formula. Under such conditions, there is no charge group exists to balance the positive charge of M because only Z carries the negative charge in the formula.

**Claim 2**, line 21, polymer represented by the second formula does not have charge. Thus, it is not encompassed by Formula I.

### ***Claim Analysis***

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## 7. Summary of Claim 1:

A redox compound having at least one state of oxidation state represented by the general formula: $\{ - [R_2 - (C=X)_{p-q} - R_1 - Z_q - R_3]_n - \} \{ 2p M^+ \}$	
X	O, NCN, or C(CN) <sub>2</sub>
Z	C-Y or N wherein Y represents O, S, NCN, -C(CN) <sub>2</sub> , with the proviso that when Y is S and n ≤ 4, X is $\text{O}^\oplus$
R <sub>1</sub>	<b>absent, O, S, NH, -(C=C)<sub>r</sub>-, -(W=W)<sub>r</sub>-</b> W independently CR <sub>6</sub> or N R <sub>6</sub> is H, halogen, CN, or C <sub>1-12</sub> alkyl, C <sub>2-12</sub> alkenyl or C <sub>6-14</sub> aryl optionally having one or more substituents of oxa, aza, or thia; and optionally 2 R <sub>6</sub> groups can be bonded to form a cycle comprising from 3 -7 members; r between 1 and 12
R <sub>2</sub>	<b>absent, a carbonated divalent radical</b> optionally substituted with aza, oxa, or thia
R <sub>3</sub>	<b>absent, a carbonated divalent radical</b> optionally substituted with aza, oxa, or thia
wherein two of R <sub>1</sub> , R <sub>2</sub> , and R <sub>3</sub> can be bonded together to form a cycle comprising 3-7 members	
q	between 0 and p
p	between 1 and 5
n	between 1 and 10 <sup>4</sup>

**Claim Rejections - 35 USC § 102**

## 8. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102

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**that form the basis for the rejections under this section made in this Office**

**action:**

**A person shall be entitled to a patent unless --  
(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.**

9. Claims 1-3 are rejected under 35 U.S.C. 102(b) as being anticipated by Shionogi & Co. Ltd. (GB 1,115,335).

Shionogi & Co. Ltd. discloses potassium rhodizonate, which is used in an antidiabetic agent (col. 1, lines 15-26). It is noted that dipotassium rhodizonate reads on the claimed compound. It is noted that Shionogi & Co. Ltd. is silent on the redox properties of these polymers. In view of the compound being identical to the claimed compound, the compound will inherit such redox properties. Thus, the present claims are anticipated by the disclosure of Shionogi & Co. Ltd.

10. Claim 1 is rejected under 35 U.S.C. 102(b) as being anticipated by Kotek et al. [Journal of Polymer Science: Polymer Chemistry Edition, **21**, 2837-2841 (1983)].

Kotek et al. disclose the following polymers (page 2838 and 2840):



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It is noted that Kotek et al. are silent on the redox properties of these polymers. In view of these polymer being identical to the claimed polymer, these polymer will inherit such redox properties. Thus, the present claim is anticipated by the disclosure of Kotek et al.

11. Claim 1 is rejected under 35 U.S.C. 102(b) as being anticipated by Tsutsumi et al. [Journal of Power Sources, **68**, 735-738 (1997)].

Tsutsumi et al. disclose the following redox polymers (page 735):

Thus, the present claim is anticipated by the disclosure of Tsutsumi et al.

12. Claim 1 is rejected under 35 U.S.C. 102(b) as being anticipated by Tsutsumi et al. [Journal of Colloid and Interface Science, **185**, 432-435 (1997)].

Tsutsumi et al. disclose the following redox polymers (page 433):

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Thus, the present claim is anticipated by the disclosure of Tsutsumi et al.

13. Claims 1-2 are rejected under 35 U.S.C. 102(b) as being anticipated by Pletcher et al. [Journal of Polymer Science: Polymer Chemistry Edition, **18**, 643-660 (1980)].

Pletcher et al. disclose poly (1,4-phenylene fumaramide) (657) and poly(1,4-phenylene methylfumaramide) (page 658). It is noted that Pletcher et al. are silent on the redox properties of these polymers. In view of these polymer being identical to the claimed polymer, these polymer will inherit such redox properties. Thus, the present claims are anticipated by the disclosure of Pletcher et al.

14. Claims 1-2 are rejected under 35 U.S.C. 102(b) as being anticipated by Speck (US 5,637,452).

Speck discloses an aqueous reagent comprising elagic acid and a metal ion such as  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{+}$ , or  $\text{Cu}^{2+}$ , which reads on the metal salt of elagic acid (abstract). It is noted that Speck is silent on the redox properties of this compound. In view of this compound being identical to the claimed compound, this compound will inherit such redox properties. Thus, the present claims are anticipated by the disclosure of Speck.

15. Claim 4 is rejected under 35 U.S.C. 102(b) as being anticipated by Fleischer (US 5,512,381).

Fleischer discloses a battery comprising an anode, a catode, and a solid state

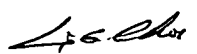
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electrolyte between the anode and the cathode, wherein the anode is composed of a material containing a proton-donating aromatic compound, the proton-donating aromatic compound being rhodizonic acid (claim 12). However, Fleischer is silent on the specific voltage required for redox couple. It is noted that the voltage for redox couple is an inherent properties of the compound at the conditions. Thus, the present claim is anticipated by the disclosure of Fleischer.

### ***Conclusion***

16. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Ling-Siu Choi whose telephone number is 571-272-1098.

If attempt to reach the examiner by telephone are unsuccessful, the examiner's supervisor, David Wu, can be reach on 571-272-1114.

  
LING-SUI CHOI  
PRIMARY EXAMINER

September 20, 2006.

<b>Notice of References Cited</b>	Application/Control No. 10/823,630		Applicant(s)/Patent Under Reexamination ARMAND ET AL.	
	Examiner Ling-Siu Choi		Art Unit 1713	Page 1 of 1

**U.S. PATENT DOCUMENTS**

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-5,637,452	06-1997	Speck, Roy E.	435/4
*	B	US-5,512,381	04-1996	Konicek et al.	428/607
*	C	US-6,743,877	06-2004	Armand et al.	526/258
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

**FOREIGN PATENT DOCUMENTS**

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N	GB 1,115,335	05-1968	Great Britain	Shionogi & Co. Ltd.	---
	O					
	P					
	Q					
	R					
	S					
	T					

**NON-PATENT DOCUMENTS**

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	Kotek et al., Journal of Polymer Science: Polymer Chemistry Edition, 21, 2837-2841(1983).
	V	Tsutsumi et al., Journal of Power Sources, 68, 735-738(1997).
	W	Tsutsumi et al., Journal of Colloid and Interface Science, 185, 432-4354(1997).
	X	Pletcher et al., Journal of Polymer Science: Polymer Chemistry Edition, 18, 643-660(1980).

\*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)  
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

1.115.335



## PATENT SPECIFICATION

DRAWINGS ATTACHED

1.115.335

Date of Application and filing Complete Specification: 5 July, 1965.

No. 28284/65.

Application made in Japan (No. 37338) on 6 July, 1964.

Complete Specification Published: 29 May, 1968.

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Index at acceptance:—C2 C(3A12A2, 3A12B5, 3A12C1, 3A12C4); A5 B2S

Int. Cl.:—C 07 c 49/60

## COMPLETE SPECIFICATION

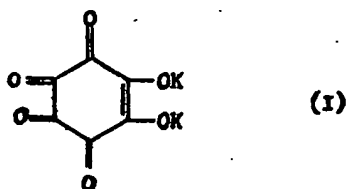
## Dipotassium Rhodizonate and the production thereof

We, SHIONOGI & Co. LTD., a Japanese Body Corporate of 12, 3-chome, Doshomachi, Higashi-ku, Osaka, Japan, and IATRO-CHEMICAL INSTITUTE OF THE PHARMACOLOGICAL RESEARCH FOUNDATION, a Japanese Body Corporate of 2—963 Daita, Setagaya-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to dipotassium rhodizonate and production thereof.

It is an object of the present invention to embody dipotassium rhodizonate as an anti-diabetic agent. Another object of this invention is to embody an improved process for preparing dipotassium rhodizonate. These and other objects will be apparent, to those conversant with the art to which the present invention pertains, from the subsequent description.

The said dipotassium rhodizonate is represented by the following formula



Rhodizonic acid and its salts are known compounds, and the known methods of synthesising them are represented as follows: (1) oxidation of inositol, hexahydroxybenzene or tetrahydroquinone; (2) reduction of triquinoyl; (3) polycondensation of glyoxal.

The first and second of the above three methods are not profitable for the mass production of rhodizonic acid because of ex-

pensiveness of the starting material and the difficulty of obtaining it on any industrial scale. The third method of polycondensing glyoxal is profitable for producing rhodizonic acid and its salts, since the starting glyoxal can be provided in large amounts and at low cost from the petrochemical industry.

As to the above third method, only polycondensing glyoxal in the presence of sodium sulfite and sodium carbonate to give sodium rhodizonate is known (U.S.S.R. Pat. No. 135,479). This method is a modification of the method of preparing tetrahydroquinone salt by condensation of glyoxal (Organic Syntheses, Vol. 42, p. 90—92 (1962)). However, in the said known method a large amount of tetrahydroxyquinone sodium salt is obtained as a byproduct besides the sodium rhodizonate in the reaction mixture owing to the solubility of sodium rhodizonate in water and the inappropriate hydrogen ion concentration of the reaction mixture. Separation and purification of the two products are difficult. Therefore, the said method is inappropriate as a process for preparing pure rhodizonic acid salt.

The present process for preparing dipotassium rhodizonate is an improvement of the said known method.

The present process comprises polycondensing glyoxal oxidatively in the presence of a potassium salt of carbonic acid and a potassium salt of sulfurous acid to prepare dipotassium rhodizonate. This process is effected ordinarily in an aqueous solvent at room temperature or while heating in aerial or oxygenic stream. At this time, the reaction mixture is kept at a hydrogen ion concentration (pH) of neutral to alkaline range, ordinarily 7.5 to 9.0, favourably 8.3 to 8.8. The terms "potassium salt of carbonic acid" and "potassium salt of sulfurous acid" are respectively intended to mean the salt generating potassium ions and carbonic ions and the salt generating potas-

[Price 4s. 6d.]

sium ions and sulfurous ions. Examples of the former are potassium carbonate and potassium bicarbonate and of the latter, potassium sulfite and potassium bisulfite. In the present process both the salts are used in combination as the reagents.

These reagents serve not only for adjustment of the hydrogen ion concentration but also for controlling oxidative condensation by oxygen. For acceleration of the reaction rate, there may be favourably used a very small amount of potassium cyanide as a catalyst. In the present process the produced dipotassium rhodizonate can be easily recovered from the reaction mixture owing to its difficult solubility in water and easy solubility of other salts.

Dipotassium rhodizonate obtained in the present process is used, as is generally known,

as a detecting reagent for a heavy metallic ion. By the studies of the present inventors, the present compound is found to be very useful as an antidiabetic drug.

Pure dipotassium rhodizonate obtained in the present invention and its derivatives (e.g. free acid, calcium salt, magnesium salt, organic base salt, etc.) show a blood sugar decreasing activity, that is, antidiabetic activity, as shown by insuline or mesoxalic acid, in biological and clinical tests. The biological and medical activities of the dipotassium salt obtained in the present process are illustratively shown as follows:

#### (I) Biological test

Blood sugar decreasing rate in mice two hours after the oral administration of dipotassium rhodizonate.

Dose (g/kg)	Number of test animals	Blood sugar decreasing rate (%)
3.1	5	-75
1.8	6	-80
1.0	8	-56
0.5	5	-32
0.3	6	-8
0.1	8	+14

#### (II) Clinical test

When 0.3 g of dipotassium rhodizonate is orally administered three times a day to a diabetic (man, 43 years old), the tendency of blood sugar value is represented by the Drawing attached hereto.

The toxicity of dipotassium rhodizonate by oral administration to mice (Lethal Dose 50) is over 6 g/kg. The present compound shows 100 times the anti-diabetic activity towards rabbits as does sodium mesoxalate, a known drug. The said pharmacological activity proves to be derived from the structure of rhodizonic acid itself and has no relation with the formation of salts.

The said dipotassium rhodizonate (I) may be administered alone or in combination with acceptable pharmaceutical carriers, the choice of which is determined by the preferred route of administration, the solubility of the substance and standard pharmaceutical practice. In general, the dosage of this substance is of approximately the same order of magnitude as the dosage of sodium mesoxalate, and the substance is useful in the treatment of the types of diabetic diseases often treated with

the known anti-diabetic agent. Examples of pharmaceutical preparations are tablets, capsules, pills, suspension and solution. In the preparation of tablets, for example, these substances may be combined with binders such as gum tragacanth, acacia, corn starch and gelatin. It is also usually desirable to have present a disintegrating agent such as, for example, corn starch, potato starch or alginic acid. Also desirable usually is a lubricant such as stearic acid, magnesium stearate or talc along with a sweetening agent such as saccharin. Flavouring agents may be also used such as peppermint, oil of wintergreen or cherry flavour. In the preparation of capsules, fillers such as enumerated above for tablets can also be used. The compositions when used in the form of suspension or solution may be combined with an aqueous sugar or sorbitol type vehicle including a viscosity control agent such as Veegum (magnesium aluminium silicate), methyl cellulose or carboxymethyl-cellulose and a suitable preservative such as sodium benzoate or parabens (methyl and propyl *p*-hydroxybenzoic acid salts). In these liquid preparations, colourings, flavourings and

buffers can also be included to produce a more pharmaceutically elegant preparation.

The compositions containing the dipotassium rhodizonate may be dispensed in dosage unit forms for a single daily therapeutic dose or in smaller units for multiple doses or in larger units for division into single doses. Parenteral compositions can also be dispensed in single units or in larger quantities from which single doses are withdrawn at the time of use.

Presently-preferred and practical embodiments of the present invention are illustratively shown in the following Examples. In these Examples, the relationship of parts by weight to parts by volume is the same as that between grams and milliliters. Temperatures are set forth in degrees centigrade.

#### EXAMPLE 1.

To distilled water (1380 parts by volume), there is added a newly prepared aqueous solution of glyoxal (40%) (345 parts by weight) at 60° C under stirring. The resultant mixture is made uniform at 60–62° C for 2 hours. After heating at 72° C once, the reaction mixture is chilled and adjusted to pH 5.6–5.8 with anhydrous potassium carbonate (18.4 parts by weight).

On the other hand, potassium cyanide (6 parts by weight) is added to a solution of potassium carbonate (390 parts by weight) and potassium sulfite (dihydrate) (291 parts by weight) in water (2000 parts by volume) and the resultant mixture warmed at 30° C.

To the said second solution, there is added dropwise the first solution at pH 8.3–8.8 in 1 hour. After finishing the dropping, the reaction mixture is stirred at 35° C for 30 minutes and allowed to stand overnight under ice-cooling. The precipitated dipotassium rhodizonate as purple-black fine crystals is collected by filtration from the reaction mixture, washed with 10% potassium acetate and cold ethanol and dried. This substance shows over 99.5% of purity after quantitative test.

#### EXAMPLE 2.

The reaction is effected as in Example 1 by using potassium bicarbonate and potassium sulfite dihydrate as the reagents for the second solution, and executed at pH 8.6 at 32–35° C. The product shows the same result of IR spectrum in comparison with pure dipotassium rhodizonate which is prepared from pure rhodizonic acid.

The following Examples illustrate the preparation of pharmaceutical products containing potassium rhodizonate as obtained above, as the active ingredient.

#### EXAMPLE 3.

Dipotassium rhodizonate (2.50 kilograms), lactose (7.47 kilograms), cornstarch (3.48 kilograms) and magnesium stearate (2.10 kilograms) are mixed together and slugged. The slugs are crushed and passed through a 30 mesh screen. The resulting granules are

mixed with magnesium stearate (2.45 kilograms) and tableted in the usual way to give 100,000 tablets. Each tablet weighing 180 milligrams contains 25.0 milligrams of the active ingredient.

#### EXAMPLE 4.

Dipotassium rhodizonate (10.00 kilograms) and lactose (20.00 kilograms) are mixed, granulated with a 10% acacia solution and dried. The granulate is forced through a 16 mesh screen and, thereafter, mixed with sodium lauryl sulfate (0.20 kilogram), magnesium stearate (1.00 kilogram) and potato starch (8.80 kilograms). The resultant mixture is tableted in the usual way to give 100,000 tablets. Each tablet weighing 40 milligrams contains 20.0 milligrams of the active ingredient.

#### EXAMPLE 5.

Dipotassium rhodizonate (125 grams) is dissolved in physiological saline solution to make 10 litres and filtered. The resultant solution is filled into 5,000 ampoules under nitrogen atmosphere and the ampoules are sterilized at 115° C for 30 minutes. Each ampoule (2 millilitres) contains 25.0 milligrams of the active ingredient.

#### WHAT WE CLAIM IS:—

1. A process for preparing dipotassium rhodizonate which comprises polycondensing glyoxal oxidatively in the presence of a potassium salt of carbonic acid and a potassium salt of sulfurous acid.

2. A process as claimed in claim 1, wherein the condensation is carried out at a pH of from 7.5 to 9.0.

3. A process as claimed in claim 1 or claim 2 wherein the glyoxal is condensed in the presence of potassium cyanide as catalyst.

4. A process for preparing dipotassium rhodizonate substantially as described herein, with reference to the foregoing Examples 1 and 2.

5. Dipotassium rhodizonate when prepared by the process claimed in any one of claims 1 to 4.

6. A pharmaceutical composition comprising dipotassium rhodizonate as claimed in claim 5, as active ingredient, together with a solid pharmaceutical carrier.

7. A composition as claimed in claim 6, wherein the carrier is one or more of gum tragacanth, acacia, corn starch, gelatin, potato starch, alginic acid, stearic acid, magnesium stearate or talc.

8. A pharmaceutical composition comprising dipotassium rhodizonate as claimed in claim 5, as active ingredient, together with a liquid pharmaceutical carrier.

9. A composition as claimed in claim 8, wherein the carrier is aqueous sugar or sorbitol or a mixture thereof.

10. A pharmaceutical composition comprising dipotassium rhodizonate as claimed

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in claim 5, as active ingredient, the composition being in the form of tablets, capsules, pills a suspension or a solution.

- 5 11. A method of treating diabetic diseases in animals other than homo sapiens which comprises the dosage administration of a pharmaceutical preparation comprising dipotassium rhodizionate as claimed in claim 5, as an active ingredient.

12. A pharmaceutical composition comprising dipotassium rhodizionate as claimed in claim 5, as active ingredient substantially as described herein with reference to the foregoing Examples 3, 4 and 5. 10

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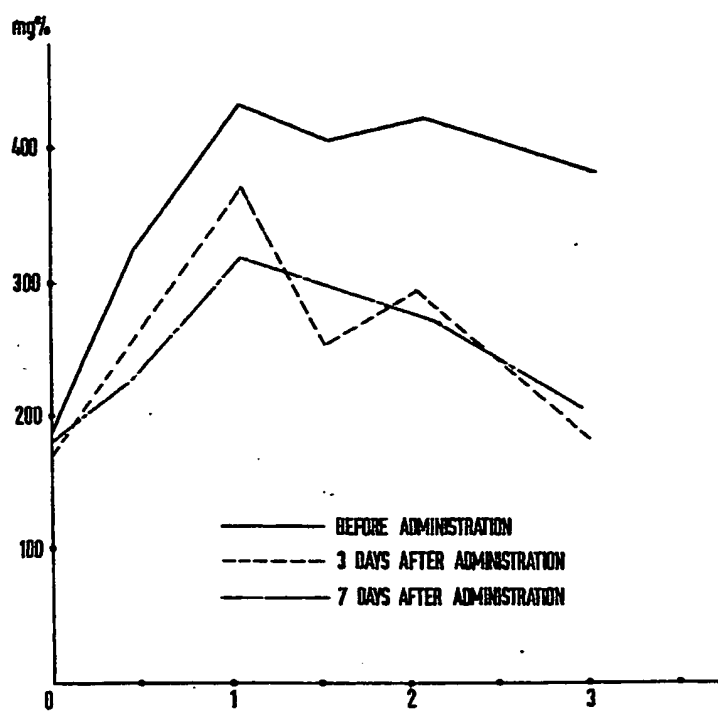
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COMPLETE SPECIFICATION

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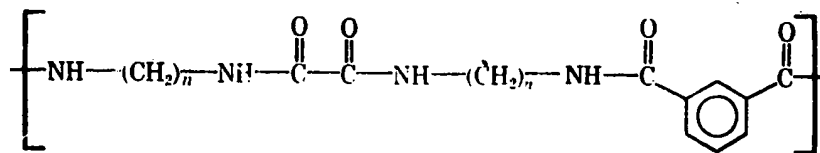
## NOTE

### **Preparation of Polyamides via the Phosphorylation Reaction. VII. Synthesis of Polyoxamides and Regular Copolyoxamides**

The Yamazaki phosphorylation reaction,<sup>1,2</sup> a useful laboratory method for the preparation of aromatic polyamides, involves a complex formed by diphenyl- or triphenylphosphite and pyridine with dicarboxylic acids in *N*-methylpyrrolidone that contains LiCl. It has been proposed that these *N*-phosphonium salts of pyridine react by aminolysis with diamines to yield polyamides. The molecular weights initially obtained were not sufficient for the preparation of commercial-quality fibers. Molecular weight limitations apparently are the result of precipitation of the polymer from the reaction medium and catalyst inactivation due to reaction with byproducts. Furthermore, a feature of the reaction is that monomers with strongly basic groups, such as aliphatic diamines, replace pyridine in the phosphite complex and lead to polymers of low molecular weight. Recently Higashi et al.<sup>3</sup> showed that poly(*p*-phenylene terephthalamide) with  $\eta_{inh} = 4.5$  dL/g can be prepared by phosphorylation reaction with triphenylphosphite in a solvent medium that contains LiCl and CaCl<sub>2</sub>. We refer to these as Higashi conditions.

In the series of articles under the present title we explored the application of the phosphorylation reaction in the preparation of wholly aromatic polyamides and polyamide-hydrazides,<sup>4</sup> modification of the procedure by incorporation of small amounts of trifunctional monomers to obtain soluble polyamides of higher molecular weight,<sup>5</sup> the synthesis of 4,4'-benzanilides,<sup>6</sup> the preparation of poly-*p*-benzamide (PBA) and *N*-methyl PBA copolymers,<sup>7</sup> the formation of nematogenic block copolymers of PBA and more flexible polyamide-hydrazide blocks,<sup>8</sup> and the formation of high molecular weight rodlike polyamides and block copolyamides.<sup>9</sup> This work demonstrates that higher molecular weights can be achieved in the phosphorylation reaction by the use of monomers that contain preformed amide linkages, presumably because of the reduction of byproducts.<sup>6,7,9</sup> It was also shown that the use of unsymmetrical monomers leads to better polymer solubility in the reaction medium, hence to higher molecular weights.<sup>6,9</sup> Finally, the different reactivities of triphenyl- and biphenylphosphite toward various monomers were exploited in a novel preparation<sup>8</sup> of block copolymers in which triphenylphosphite is used to polymerize the first monomer and the diphenylphosphite byproduct is used as a catalyst for polymerization of the second monomer.

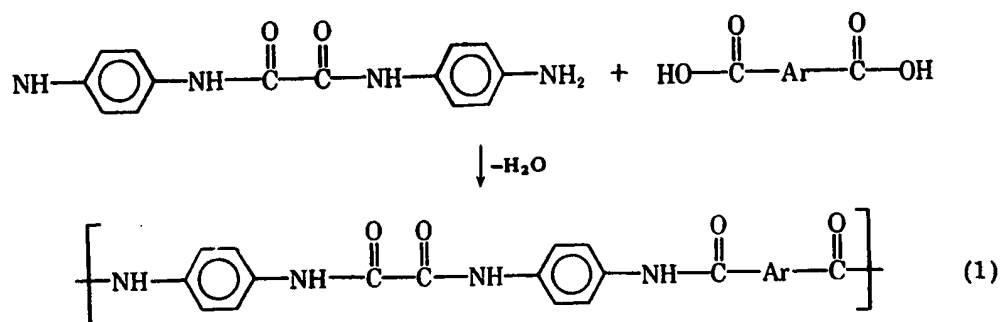
Polyoxamides can be prepared by the Schotten-Baumann reaction with liquid-liquid interfacial,<sup>10,11</sup> gas-liquid interfacial,<sup>10-13</sup> or solution<sup>10,11,14-16</sup> polycondensation techniques. These polymers can also be produced by the reaction of lower alkyl esters of oxalic acid with strongly basic diamines.<sup>10,17</sup> The Schotten-Baumann method produces aromatic copolyoxamides of sufficient molecular weight to form fibers of commercial quality.<sup>15,16</sup> It has also been used for the synthesis of a number of aliphatic and regular aliphatic/aromatic copolyoxamides; for example, the copolyoxamides



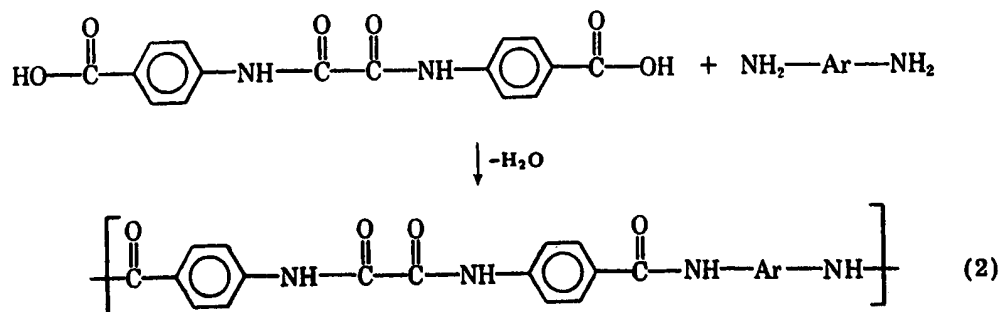
synthesized in this way were effective materials for desalination membranes when  $n = 2$  to 4.<sup>18</sup> The second method involving esters is restricted to aliphatic polyoxamide homopolymers.

The synthesis of polyamides from oxalic acid and diamines by the phosphorylation reaction was reported by Yamazaki and Higashi<sup>19</sup> to yield no polymer. One of the present authors<sup>20</sup> essentially confirmed this report by finding that the reaction of oxalic acid and 4,4'-methylenedianiline yielded only 40% of a polymer with  $\eta_{inh} = 0.1$  dL/g. Yamazaki reported that oxalic and malonic acids are decomposed under the conditions of the phosphorylation reaction (presumably due to anhydride formation), whereas succinic acid forms succinimides.<sup>19</sup> As mentioned above, we have found that polymers of higher inherent viscosity can be obtained in the phosphorylation reaction by the use

of monomers that contain performed amide linkages. Certain linkages that normally cannot be formed in the phosphorylation reaction, such as an ester, can also be incorporated into ordered ester-amide copolymers by the reaction of a diacid with a diamine that contains an internal ester linkage.<sup>4</sup> Likewise, moieties such as glycine were incorporated into an ordered copolyamide by preforming a diacid that contained a bis-glycineamide linkage.<sup>4</sup> Finally, oxalyhydrazide was reacted with terephthalic acid to yield an ordered polyhydrazide.<sup>4</sup> Undoubtedly, the preparation of this polymer by the phosphorylation reaction was made feasible by preformation of the oxalic moiety within the hydrazide linkage. This note reports the results of the application of this technique to the preparation of regular copolyoxamides, as illustrated by the following reaction schemes:



and



## EXPERIMENTAL

### Monomers

Isophthalic (IPA) and terephthalic acid (TPA) used were of fiber-grade purity. 4,4'-Dicarboxyoxanilide (DCA) with mp >350°C was prepared by reacting 2 mol of *p*-aminobenzoic acid with 1 mol of oxalyl chloride.

ANAL. Calcd for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>: C = 58.54%, H = 3.68%, N = 8.53%. Found: C = 58.67%, H = 3.87%, N = 8.73%

4,4'-Diaminoxanilide (DAO) was made by the Dobinson procedure<sup>15</sup> (mp 278–279.5°C). 4,4'-Diaminobenzanilide (DAB) was prepared as reported.<sup>9</sup> *p*-Phenylenediamine (PPD) (Fisher Scientific Company) and 4-aminooxanilic acid (AOA) (Aldrich Chemical Company) were used without further purification.

### Polymerization

The polyoxamides coded (1)–(6) in Table I were synthesized by the optimum procedures reported for polyamides by Yamazaki et al.<sup>2</sup> and Higashi and co-workers.<sup>3</sup> Only polymer (3), polymerized under Higashi conditions, remained completely soluble in the reaction medium. In all other cases the polymer precipitated after 5–20 min of reaction. Nevertheless, polymer yields were nearly quantitative in all cases.

## RESULTS AND DISCUSSION

The inherent viscosities of the polyoxamides prepared by the phosphorylation reaction are compared in Table I with values reported in the literature for polymers prepared by gas-liquid interfacial

TABLE I  
Characterization of Polyoxamides

No.	Conditions <sup>a</sup>	Structure	Exp. $\eta_{inh}^b$	$\frac{Lit. \eta_{inh}}{I^c}$	S <sup>c</sup>
1	H Y		0.13 0.17	0.8-1.1	
2	H Y		0.18 0.37		3.1 <sup>15</sup>
3	H Y		0.18 0.52		0.6 <sup>15</sup>
4	H		0.59		
5	H		0.52		4.1 <sup>16,d</sup>
6	H		1.15		

<sup>a</sup> H = Higashi conditions, Y = Yamazaki conditions.

<sup>b</sup> Inherent viscosity measured at 25°C for 0.2 g/dL solutions in H<sub>2</sub>SO<sub>4</sub>.

<sup>c</sup> I—gas (oxalyl chloride)—liquid interfacial polycondensation. S—solution polycondensation in amide type solvents containing dissolved inorganic salt.

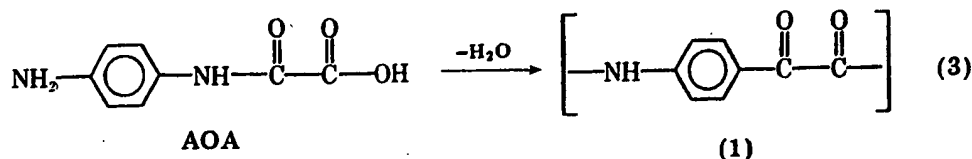
<sup>d</sup> Intrinsic viscosity.

TABLE II  
Inherent Viscosities of Random Copolymers of Terephthalic and Isophthalic Acids With DAO

Mol IPA	$\eta_{inh}$
0	0.18
10	0.20
25	0.24
50	0.43 (0.7) <sup>a</sup>
100	0.18

<sup>a</sup> Data of Dobinson<sup>15</sup> for copolymer made by solution polycondensation of DAO with terephthaloyl and isophthaloyl chlorides.

or solution polymerization. In general, the polyoxamides prepared by the phosphorylation reaction have lower inherent viscosities, probably because of low solubility in the reaction medium. The inherent viscosities of polymer (1), prepared under Higashi and Yamazaki conditions, were only 0.13 and 0.17 dL/g, respectively. This polymer has the shortest repeating unit and might be expected to be the least soluble. It should be noted, however, that the yield of polymer was quantitative, according to the reaction



Only a 15% yield of polymer with  $\eta_{inh} = 0.07$  dL/g was obtained in an attempt to prepare (1) from an equimolar mixture of oxalic acid and PPD. This provides another example in which the use of monomers with preformed linkages can be used to protect a group that would otherwise decompose under the reaction conditions and lead to improved yields and higher inherent viscosities.

Regular copolyamides (2)–(6) provide further illustrations of the use of preformed linkages to avoid decomposition under these reaction conditions. The yields were nearly quantitative and polymers of moderate to high  $\eta_{inh}$  were obtained. Moreover, these polymers have longer repeating units and might therefore be less likely to crystallize from solution. In general, this expectation is borne out by the higher inherent viscosities of these polymers. Incorporation of isophthalic acid would also be expected to give a more soluble polymer. As mentioned above, polymer (3) remained soluble during polymerization under Higashi conditions. Unfortunately, these conditions are known to be ineffective for the preparation of polyamides that involve isophthalic acid; therefore the low inherent viscosity is not surprising. In fact, the low  $\eta_{inh}$  may explain in part why the polymer remained soluble. The inherent viscosity achieved for polymer (3) under Yamazaki conditions is comparable to the value reported by solution polymerization.<sup>15</sup> The highest  $\eta_{inh}$  value obtained by the phosphorylation reaction is shown by polymer (6), which would be expected to have better solubility because of the long repeating unit and lack of symmetry of the DAB unit.

We also prepared several random copolymers of TA and IPA with DAO under Higashi conditions. As shown in Table II, the inherent viscosities of these copolymers are low. The increase in  $\eta_{inh}$  on passing from 0 to 50% IPA may be somewhat surprising because Higashi conditions are generally not effective for isophthalic acid.

We investigated the ability of regular copolyamide (6) to form a lyotropic nematic phase. Only isotropic solutions were found in *N*-methylpyrrolidone that contained 4% LiCl up to the solubility limit, 10% by weight. Polymer (6) formed an anisotropic phase in 100% H<sub>2</sub>SO<sub>4</sub> when the concentration exceeded 12% by weight.

## SUMMARY

Polyoxamides of low-to-moderate molecular weight can be prepared in quantitative yields by the phosphorylation reaction under Yamazaki or Higashi conditions, provided that the oxamide group is preformed in a diacid or diamine monomer. An AB type monomer, 4-aminooxanilic acid, also

can be used to make poly-(*p*-phenyleneoxamide) in quantitative yield, whereas the reaction of oxalic acid and *p*-phenylenediamine results in only a 15% yield under the same conditions. The polyoxamides prepared by the phosphorylation reaction generally have lower inherent viscosities than those obtained by polycondensation of oxalyl chloride with diamines or of aromatic diacid chlorides with diamines that contain the oxamide group. The probable reason for this finding is the poor solubility of the polyoxamides in the phosphorylation medium. Only in polyoxamide derived from 4,4'-diaminooxanilide and isophthalic acid did the two procedures yield comparable inherent viscosities. A wholly para-oriented polyoxamide with  $\eta_{inh} = 1.15$  dL/g gave an anisotropic phase in 100% sulfuric acid for polymer concentrations above 12% by weight.

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Various polyamides containing a disulfide bond in their main chain were prepared by condensation of a diacid, 3,3'-dithiodipropionic acid (P), 6,6'-dithiodinicotinic acid (N), or 2,2'-dithiodibenzoic acid (B) and a diamine, alkyldiamine (I, II, III, and IV:  $\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2$ ,  $n=6, 8$ , and 12) or cystamine, V:  $\text{NH}_2-(\text{CH}_2)_2-\text{S}-\text{S}-(\text{CH}_2)_2-\text{NH}_2$ . Polyamides P-I, P-II, P-III, P-IV, and P-V were insoluble in common organic solvents, but soluble in formic acid or trifluoroacetic acid. Polyamides containing N or B as the acid moiety, i.e. aromatic polyamides, were soluble in  $N,N'$ -dimethylformamide or dimethyl sulfoxide. The electrochemical behavior of P-II electrode in the organic electrolytes, such as propylene carbonate (PC), PC-1,2-dimethoxyethane (DME) mixture, ethylene carbonate (EC)-DME mixture, which are used as the electrolytes for common lithium batteries was investigated. In the mixed electrolyte, PC-DME (1:1, by volume) a good electrochemical response of P-II electrode based on the redox of disulfide bonds in the polymer was observed. Charge/discharge cycling tests of Li/P-II cells were also performed. At the first discharge, the net capacity of the cell was  $97.5 \text{ Ah kg}^{-1}$  (this value was calculated from the weight of loaded P-II on the electrode). Utilization of P-II was 53%. Cell capacity versus cycle number was also investigated. © 1997 Elsevier Science S.A.

**Keywords:** Disulfides; Positive active materials; Polyamides; Secondary batteries

Various organic compounds containing disulfide bonds, organosulfur compounds, are one of the most attractive and interesting candidates' groups of positive active materials for high-energy storage secondary lithium batteries [1-11]. Their theoretical capacity is very high, for example, the theoretical capacity of 2,5-dimercapto-1,3,4-thiadiazole is about  $400 \text{ Ah kg}^{-1}$ . Furthermore, the redox reaction of organosulfur compounds,  $\text{R-S-S-R} + 2e^- = 2(\text{RS}^-)$ , is usually reversible where R represents an organic moiety. The reactivity, solubility, and electrical capacity of the organodisulfides depend on the structure of R. The design of the R moiety is a key point for the application of these compounds in the active material for secondary batteries. Previously, we reported the preparation of polyamides containing disulfide bonds and their electrochemical behavior in acetonitrile electrolyte solution [10,11]. All polyamides were prepared by the condensation of an acid dichloride and a diamine with the interfacial polymerization technique. We produced various polyamides containing a disulfide bond and different R moieties. Selecting a pair of diacid and diamine. Fig. 1 shows

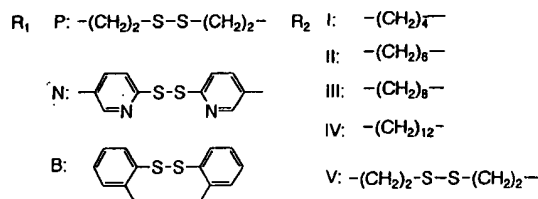
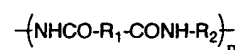


Fig. 1. Structure of various polyamides containing a disulfide bond.

**Table 1**  
**Theoretical capacity (Ah kg<sup>-1</sup>) of polyamides containing disulfide bond**

Diacid <sup>a</sup>	Diamine <sup>a</sup>				
	I	II	III	IV	V
P	204	185	168	143	328
N	148	138	129	113	253
B	150	139	129	114	254

<sup>a</sup> Detail structures are presented in Fig. 1.

structures of the polyamides; their theoretical electric capacity was listed in Table 1. Acids used for preparation of polyamides were 3,3'-dithiodipropionic acid (P), 6,6'-

Responding author.

dithiodinicotinic acid (N), or 2,2'-dithiodibenzoic acid (B). Diamine was alkyldiamine (I-IV:  $\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2$ ,  $n = 4, 6, 8, 12$ ), or cystamine V:  $\text{NH}_2-(\text{CH}_2)_2-\text{S}-\text{S}-(\text{CH}_2)_2-\text{NH}_2$ . All polyamides were prepared by condensation of the corresponding acid dichloride and the corresponding diamine with the interfacial polymerization technique.

In this study, we report the redox behavior of the polymers in organic electrolyte solutions, especially polyamide P-II, and the charge/discharge behavior of the model, Li/P-II cell.

## 2. Experimental

### 2.1. Materials

3,3'-dithiodipropionic acid (Aldrich), 6,6'-dithiodinicotinic acid (Aldrich), 2,2'-dithiodibenzoic acid (Ishizu), thionyl chloride (Ishizu), various alkyldiamines, ( $\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2$ ,  $n = 4, 6, 8, 12$ , Ishizu), cystamine (Ishizu), and acetonitrile (HPLC grade, Ishizu) were used as received. The solvents for electrolyte solution were propylene carbonate (PC), a 1:1 (by volume) mixture of PC and 1,2-dimethoxyethane (DME), ethylene carbonate (EC), and a 1:1 (by volume) mixture of EC and DME, which were used as received (Mitsubishi Petrochemical, battery grade). Lithium perchlorate trihydrate (Ishizu) was dried at 150 °C for 24 h to remove hydrated water. Graphite powder (Wako) was also used as received.

### 2.2. Preparation of polyamides

Polyamides were prepared by condensation of the corresponding acid and diamine with the interfacial polymerization technique. The typical preparation procedure was as follows: a mixture of 2.5 g of 3,3'-dithiodipropionic acid (12 mmol) and 10.0 ml of excess thionyl chloride was heated under reflux for 90 min. After cooling the mixture to room temperature, excess thionyl chloride was removed by using a rotary evaporator. The oily acid chloride was dissolved with 100 ml of  $\text{CCl}_4$  or  $\text{CHCl}_3$ . Corresponding diamine (12 mmol) was dissolved into a sodium hydroxide aqueous solution (1.92 g, 48 mmol/100 ml). The diamine aqueous solution was gradually added to the acid chloride/ $\text{CCl}_4$  or  $\text{CHCl}_3$  solution. Polyamide was formed at the  $\text{H}_2\text{O}/\text{CCl}_4$  or  $\text{CHCl}_3$  interface. The resulted polymer was collected, washed with ethanol, water, and ethanol, and dried under vacuum over 24 h at room temperature. The structure of polyamides was confirmed by IR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR measurements.

### 2.3. Electrochemical measurements

Electrochemical measurements for polyamides were performed with a conventional three-electrode cell. The working electrode was a carbon-paste electrode [10-15]. The configuration of the working electrode was reported in our previous paper [10]. Prepared polyamide electrode is the mixed carbon-paste electrode. A mixture of polyamide, graphite powder, and a small amount of the electrolyte solution was blended in a mortar and the paste was loaded on the glassy

carbon electrode; the top of the electrode was covered with a polypropylene separator sheet to hold the paste on the electrode. The electrode is called polyamide electrode, for example, P-II electrode. Usual paste for polyamide electrode was prepared by mixing polyamide and graphite in a weight ratio of 1:1. Unless otherwise stated, the concentration of  $\text{LiClO}_4$  was  $0.1 \text{ mol dm}^{-3}$ . All solutions for electrochemical measurements were degassed with argon for 30 min prior to use. In cyclic voltammetry measurements a potentiogalvanostat (HA-301, Hokuto), a function generator (HB-104, Hokuto) and an x-y recorder (WX-1100, Graphtec) were used. The electrode potentials cited in this paper are referred to an  $\text{Li}/\text{Li}^+$  electrode.

Cycling tests of the model cell were performed with a charge/discharge controller (HJ-201, Hokuto Denko) and an x-t recorder (Type 3057, Yokokawa).

## 3. Results and discussion

### 3.1. Structure and properties of polyamides containing disulfide bond

The structure of polyamides are presented in Fig. 1.

All polymers have disulfide bonds in their main chain. The distance from one disulfide bond to the next one is different in polyamides studied. Among the polyamides, the distance in P-II is the shortest and in polyamide P-IV the longest. All polyamides are colorless and odorless powders, and stable in air. The polyamides containing P as the acid moiety, P-I, P-II, P-III, P-IV, and P-V, are insoluble in usual organic solvents, such as acetonitrile, alcohol, acetone, and ether. They are soluble in formic acid and trifluoroacetic acid. The aromatic polyamides containing N or B as acid moiety are soluble in N,N'-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The structure of polyamides was confirmed by IR,  $^1\text{H}$ -, and  $^{13}\text{C}$  NMR spectroscopy. For example, the IR spectrum of P-II showed bands at  $1640 \text{ cm}^{-1}$  and  $1550 \text{ cm}^{-1}$  which are attributed to the amide I and amide II bands, respectively [16]. NMR results for the polyamides also supported the structure as presented in Fig. 1.

### 3.2. Electrochemical behavior of polyamides containing disulfide bond in organic electrolyte

Fig. 2 shows the cyclic voltammograms for a P-II electrode in various organic electrolyte solutions containing  $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$ . The mixing weight ratio of P-II and graphite was 1:1. The counter electrode was a lithium foil, and the reference electrode was a lithium tip ( $\text{Li}/\text{Li}^+$ ). The electrode potentials cited in this section are referred to the  $\text{Li}/\text{Li}^+$  electrode.

As shown in Fig. 2(a), the increase in cathodic current was observed from 2.0 to 1.3 V in the first negative scan. In the positive scan the anodic peak at 2.9 V was observed. The increase in cathodic current is due to the reduction of disulfide bonds in the polyamide and the anodic peak arises from the oxidation of thiol or thiolate to disulfide. However, the quan-



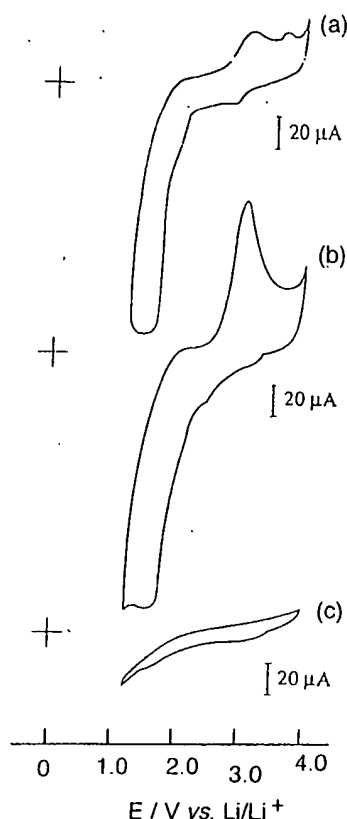


Fig. 2. Cyclic voltammograms of P-II electrode in various organic electrolytes containing  $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$ . Scan rate  $0.5 \text{ mV s}^{-1}$ . Mixing ratio of P-II and graphite is 1:1, by weight. Counter electrode: Li foil; reference electrode: Li tips ( $\text{Li/Li}^+$ ). (a) PC, (b) PC-DME (1:1, by volume), and (c) EC-DME (1:1, by volume).

of electricity estimated from the anodic peak area is smaller than that from the cathodic area. This suggests that P-II is not preferable to use as the positive material in the PC electrolyte. Fig. 2(c) shows the voltammogram of the P-II electrode in EC-DME (1:1, by volume) electrolyte. In this electrolyte solution, any obvious current peak or increase in current was not observed. The EC-DME mixed electrolyte solution interferes the redox of disulfide in P-II. Fig. 2(b) shows the voltammogram of the P-II electrode in PC-DME (1:1, by volume) electrolyte. The increase in cathodic current in the negative-going scan was observed to be similar as in the PC electrolyte. An anodic peak at  $2.9 \text{ V}$  in the positive scan was observed. The anodic peak current was larger than that in the PC electrolyte. Therefore, PC-DME (1:1, by volume) mixed electrolyte is suitable as an electrolyte for the P-II electrode. The reason is not clear. It may be concerned with the stability of the thiolate anion in the electrolyte and/or suppression of side reactions of P-II and its derivatives in the electrolyte.

#### (b) Charge/charge behavior of Li/P-II model cell

The model cell, Li/P-II cell, was fabricated and the cycling performance of the cell was demonstrated. The configuration of the positive electrode and the cell in the model cell was

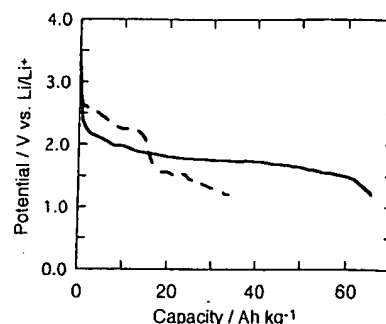


Fig. 3. First discharge curves of an (—) Li/P-II cell and (---) Li/graphite cell. Electrolyte  $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC-DME}$  (1:1, by volume). Electrodes: P-II electrode, P-II  $46.5 \text{ mg}$  and graphite  $46.5 \text{ mg}$ ; graphite electrode, graphite  $47.0 \text{ mg}$ . Electrolyte:  $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC-DME}$  (1:1, by volume). Current density:  $500 \mu\text{A g}^{-1}$  ( $5.3 \times 10^{-3} \text{ C}$  in the case of the Li/P-II cell). Cutoff voltage  $1.2 \text{ V}$ .

same as that for the cyclic voltammetric measurements. The potential was referred to the reference electrode.

Fig. 3 shows the first discharge curves of the Li/P-II cell and Li/graphite cell. The Li/graphite cell was used to estimate the net capacity of the P-II electrode. The current density was  $500 \mu\text{A g}^{-1}$  per gram of positive electrode, and the cutoff voltage was  $1.2 \text{ V}$ . The potential of the Li/P-II cell decreased from  $4.0$  to  $2.4 \text{ V}$ , rapidly at the initial stage of the discharge process. After this process, the potential of the cell decreased gradually. The first discharge capacity of the Li/P-II cell was  $66.0 \text{ Ah kg}^{-1}$  (per kilogram of P-II electrode, the mixed ratio of P-II and graphite is 1:1, by weight). The discharge capacity of the Li/graphite cell was  $34.5 \text{ Ah kg}^{-1}$  (per kilogram of graphite electrode). Thus P-II polymer in the cell acted as a positive active material. The net capacity of the P-II electrode based on the weight of P-II was  $97.5 \text{ Ah kg}^{-1}$ . The theoretical capacity of the polyamides was  $185 \text{ Ah kg}^{-1}$  (see Table 1). The P-II utilization was 53%.

Fig. 4 shows the variation of discharge capacity for the Li/P-II and Li/graphite cells versus cycle number.

The capacity of the Li/P-II cell decreased gradually with the cycle number. However, the capacity of Li/graphite cell also decreased to about  $2\text{--}3 \text{ Ah kg}^{-1}$ . The further observed cell capacity of the Li/P-II cell after the first discharge was

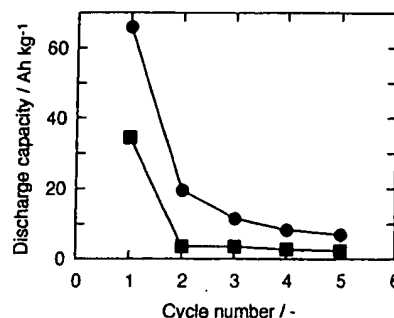


Fig. 4. Variation of discharge capacities (per kilogram of loaded electrode material paste) for (●) Li/P-II cell and (■) Li/graphite cell with cycle number. Electrode: P-II electrode, P-II  $46.5 \text{ mg}$ ; graphite  $46.5 \text{ mg}$ , graphite electrode, graphite  $47.0 \text{ mg}$ . Electrolyte:  $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC-DME}$  (1:1, by volume). Current density:  $500 \mu\text{A g}^{-1}$  (per gram of polyamide and graphite). Potential range:  $1.2\text{--}4.0 \text{ V}$  (vs.  $\text{Li/Li}^+$ ).

based on the redox reaction of P-II. Optimization of various conditions, such as the configuration of the electrode, the mixing ratio of conductive material and P-II, current density, should be performed in order to apply P-II and other polyamide materials in practical lithium batteries.

Other polyamides have been prepared and investigation of their electrochemical behavior is now in progress.

### Acknowledgements

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Abstract

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Introduction

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# Preparation and Characterization of New Self-Assembled Polyamide Film Containing Disulfide Bonds on Gold Electrode

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New polyamides containing disulfide bonds in their main chains are prepared by condensation between 3,3'-dithiodipropionic acid and various alkyldiamines ( $\text{NH}_2\text{-(CH}_2\text{)}_n\text{-NH}_2$ ,  $n = 4$  and 12, polyamide I and II). The polyamides form a thin layer on a gold substrate. The surface of polyamide modified electrodes were investigated by AFM and XPS measurements. The surface structure depends on the polyamide structure, especially alkyl chain length of the polyamide. Furthermore, adsorption of ferrocene derivatives [1-ferrocenylmethanol (FME) or 2-amino-3-ferrocenylpropionic acid (AFP)] on the polyamide modified electrodes and their electrochemical responses were investigated. Interaction between the polyamide on the electrode and the ferrocene derivatives depends on the structure of the ferrocene derivatives and polyamide chain length.

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**Key Words:** polyamide; modified electrode; ferrocene derivative; redox reaction.

molecules on the substrate or with other molecules in the solution. Therefore, the polymers may provide multifunctionalized surfaces with easy preparation.

In this paper we describe the preparation and adsorption of new types of polyamides which contain disulfide bonds in their main chains. Furthermore, the adsorption behavior of ferrocene derivatives on the polyamide modified surface is also investigated. The ferrocene derivatives are 1-ferrocenylmethanol (FME) and 2-amino-3-ferrocenylpropionic acid (AFP), which have interactive functional groups with amide bonds. Amide bonds in the polymer chain will act as interactive sites with hydroxyl, carbonyl, or amino groups in the ferrocene derivatives through the formation of hydrogen bonds. Adsorption behavior the ferrocene derivatives on the polyamide modified surface is estimated from voltammetric responses of the adsorbed ferrocene derivatives on the polyamide modified surface.

## INTRODUCTION

An organosulfur compound which has a disulfide bond or thiol group forms a self-assembled mono- or multilayer on a gold substrate when the substrate is dipped into its dilute solution (1–11). Alkanethiol with a long alkyl chain provides a stable, well-oriented monolayer on gold or other metal surface. Self-assembled layers prepared in this manner have been used to create functionalized surfaces, for example, modified electrode (12–16), for ion or molecular recognition (17–19). Organosulfur polymer modification on gold has been also investigated (20–24). However, the main chain structure of the polymers was a methylene backbone,  $\text{-(CH}_2\text{-CHX-)}_n\text{-}$  or  $\text{-(CH}_2\text{-CXY-)}_n\text{-}$ , such as poly(methyl methacrylate), poly(methacrylic acid), or poly(acrylic acid) (20–22), or a rigid backbone, such as poly(*p*-phenylene) (23) or diacetylene (24). As far as we know, few condensation polymers for self-assembling modification, such as polyester and polyamide, have been reported (25). Polyester and polyamide have functional groups, the ester bond and the amide bond, respectively, which can interact with other atoms or

## EXPERIMENTAL

### Materials

3,3'-Dithiodipropionic acid (Aldrich), *n*-alkyldiamines (Ishizu), and other reagents were purchased and used as received. Ferrocene derivatives 1-ferrocenylmethanol (FME) and 2-amino-3-ferrocenylpropionic acid (AFP) were synthesized following the literature (26, 27).

### Preparation of Polyamides Containing Disulfide Bonds

Polyamides containing disulfide bonds were prepared by condensation between 3,3'-dithiodipropionic acid and corresponding diamine with interfacial polymerization technique. Figure 1 shows the structures of polyamides I and II. A typical preparation procedure was as follows: A mixture of 2 g of 3,3'-dithiodipropionic acid (9.5 mmol) and 10 ml of thionyl chloride was heated at 100°C for 90 min to prepare acid chloride. After the heating, the excess thionyl chloride was removed from the mixture. The oily acid chloride was dissolved with 100 ml of  $\text{CHCl}_3$ . The corresponding *n*-alkyldiamine (9.5 mmol) was dissolved into 100 ml of aqueous sodium hydroxide solution (NaOH, 0.8 g, 20 mmol). The

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alkyldiamine aqueous solution was slowly added to the acid chloride/ $\text{CHCl}_3$  solution not to perturb the interface. Polyamide was formed at the  $\text{H}_2\text{O}$ /organic solution interface. The resulting polymer was collected, washed with water, and dried under vacuum for 24 h at room temperature. The polymer was reprecipitated from trifluoroacetic acid/methanol. The structure of polyamides was confirmed by IR and  $^1\text{H}$ -NMR measurements.

**Polyamide I.**  $^1\text{H}$  NMR (trifluoroacetic acid- $d$ ) (270 MHz):  $\delta$  3.83 (s, 4H,  $-\text{S}-\text{CH}_2-$ ), 3.22–3.55 (m, 10H,  $-\text{HNCOCH}_2-$ ,  $-\text{CH}_2\text{CO}-$ ), 2.09 (d, 4H,  $-\text{CH}_2\text{CH}_2-$ ). IR (KBr disk):  $1650\text{ cm}^{-1}$  (amide I),  $1550\text{ cm}^{-1}$  (amide II).

**Polyamide II.**  $^1\text{H}$  NMR (trifluoroacetic acid- $d$ ) (270 MHz):  $\delta$  4.2–4.29 (m, 4H,  $-\text{S}-\text{CH}_2-$ ), 3.62–3.95 (m, 10H,  $-\text{HNCOCH}_2-$ ,  $-\text{CH}_2\text{CO}-$ ), 2.44 (d, 4H,  $-\text{NHCH}_2-\text{CH}_2-$ ), 2.02 (s, 16H,  $\text{CH}_2$ ). IR (KBr disk):  $1650\text{ cm}^{-1}$  (amide I),  $1550\text{ cm}^{-1}$  (amide II).

#### Preparation of Polyamide Modified Electrode

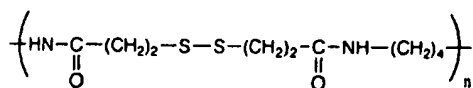
A gold sputtered glass plate was dipped into a  $10\text{ mmol dm}^{-3}$  polyamide/trifluoroacetic acid or formic acid solution for 24 h at room temperature ( $20$ – $25^\circ\text{C}$ ), and then the plate was washed with trifluoroacetic acid or formic acid and water (purified by a Milli-Q purifying system) repeatedly to remove excess adsorbed polyamide.

#### Modification of Ferrocene Derivatives on Polyamide Modified Electrode

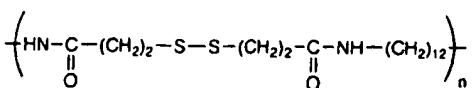
A polyamide modified electrode was dipped into a  $1\text{ mmol dm}^{-3}$  ferrocene derivative/methanol solution for 24 h at room temperature ( $20$ – $25^\circ\text{C}$ ), and then the plate was washed with methanol repeatedly to remove excess adsorbed ferrocene derivative. FME/polyamide I electrode means the FME adsorbed polyamide I modified electrode. Other electrodes are also presented in a similar manner.

#### Measurements

AFM images of electrode surfaces were obtained with a Nanoscope II (Digital Instruments, Inc.) utilizing an optical level in combination with a microfabricated  $\text{Si}_3\text{N}_4$  tip and



polyamide I



polyamide II

FIG. 1. Structures of polyamide I and II.

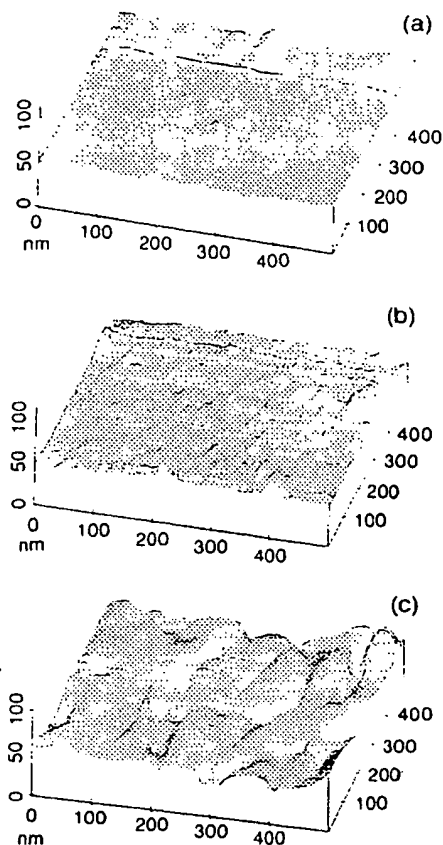


FIG. 2. AFM images of  $500\text{ nm} \times 500\text{ nm}$  section of a gold sputtered film (a), polyamide I modified electrode (b), and polyamide II modified electrode (c). Measurement conditions: Z,  $84.5\text{ \AA/V}$ , XY,  $68.1\text{ \AA/V}$ , input filter off, high-pass filter off, low-pass filter off, and scan rate  $1.02$ – $2.02\text{ Hz}$ .

cantilever (force constant  $k = 0.12\text{ N m}^{-1}$ ). XPS measurements of electrode surfaces were performed with a ESCA-LAB 210 (Fisons Surface Science). The  $\text{Mg } \alpha$  line was used. Electrochemical responses of the modified electrode were recorded with a potentiogalvanostat (HA-301, Hokuto), a function generator (HB-103, Hokuto), and an X-Y recorder (XY-1000, Graphtec). The electrochemical cell was a convenience three-electrode cell, which had a counter electrode (Pt plate,  $2.5\text{ cm} \times 2.5\text{ cm}$ ) and a reference electrode (saturated calomel electrode). The apparatus surface area of working electrode was  $0.5\text{ cm}^2$  ( $1\text{ cm} \times 0.5\text{ cm}$ ). All of the electrode potentials cited in this paper are referred to SCE. The electrolyte solution was pH 6.0 buffered solution containing sodium hydroxide and potassium hydrogen phthalate. All solutions for electrochemical measurements were degassed with Ar for 30 min prior to use.

## RESULTS AND DISCUSSION

### Surface Structure of Polyamide Modified Electrode

Figure 2 shows AFM images of non-modified, polyamide I or polyamide II modified gold surface. A gold sputtered

TABLE I

Atomic Composition and Ratio of a Polyamide Layer (Polyamide I or II) on a Gold Surface, Derived from Angle-Dependent XPS

Element (%) or ratio of elements	Take off angle					
	Polyamide I			Polyamide II		
	90°	35°	15°	90°	35°	15°
C	37.8	49.7	68.4	78.5	80.9	85.3
N	2.8	3.3	3.5	5.6	7.0	4.8
O	9.7	12.9	15.0	9.5	7.2	6.3
S	2.4	4.7	2.3	5.3	4.4	3.5
Au	47.3	29.4	10.8	1.0	0.4	0.0
C/N	13.5	15.1	19.5	14.0	11.6	17.8
C/O	3.9	3.9	4.6	8.3	11.2	13.5
C/S	15.8	10.6	29.7	14.8	18.4	24.4

Note. Theoretical values of polyamide I ( $C_{16}H_{18}N_2O_2S_2$ ), C/N, 5; C/O, 5; C/S, 5, and polyamide II ( $C_{18}H_{24}N_2O_2S_2$ ), C/N, 9; C/O, 9; C/S, 9.

surface on the glass plate was initially imaged before the modification (Fig. 2(a)). The image contains regions or domains of smooth surface and some convex shape parts *ca.* 10 nm in height and 20 nm in width. As shown in Fig. 2(b), polyamide I modified electrode had similar structure of a naked gold surface. However, some line shape structure was observed. The number of convex region increased. It suggests that polyamide I molecules are adsorbed on the gold surface and the adsorbed polymer chain should be extended on the substrate. Figure 2(c) shows the image of polyamide II modified electrode surface. A very rough surface was created by the polyamide II modification. The size of the convex was *ca.* 50–100 nm. It suggests that polyamide II was adsorbed on the Au surface aggregated and/or stacked form. The AFM images of polyamide modified electrodes suggest that polyamide I exists in the extended form and that polyamide II has a globular or tangled form on the electrode.

XPS measurements were also performed to study the surface analysis of polyamide modified electrodes. These spectra confirm the presence of the desired elements in the polyamide layers and allow to us calculate their atomic composition. Typical results of XPS measurements for polyamide I and II modified gold substrates are listed in Table I. Tilt angle of a sample with X-ray beam was set at 15°, 35°, and 90°. Through the angular-dependent studies, a depth profile of the surface region was also provided. The values of C/N, C/O, and C/S of polyamide I increased with decrease in the tilt angle. It suggests that S, N, and O atoms in the polymer I exist on the surface and that C atoms exist over the electrode surface. On polyamide II modified electrode, S, N, and O atoms also exist on the surface while C atoms and methylene chains stay over the surface. This indicates

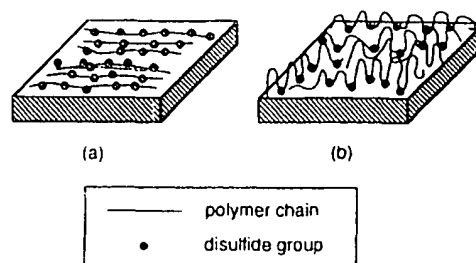


FIG. 3. Schematic presentation of the surface of polyamide I (a) and II (b) modified electrodes. Solid dots represent the disulfide groups in the polymer chain.

that the methylene groups in the polymer chains are probably distributed uniformly in the polymer layer. Schematic diagrams of polyamide modified electrodes are shown in Fig. 3. Fig. 3(a) shows the image of polyamide I modified electrode. From the results of AFM and XPS measurements polyamide I chains on the surface exist as their extended form. Polyamide II chains on the gold surface form globular or entangled structures on the gold plate as shown in Fig. 3(b).

#### Adsorption of Ferrocene Derivatives on the Polyamide Modified Electrode

Figures 4 and 5 shows the voltammetric responses of the polyamide modified electrode with adsorbed ferrocene derivative, FME or AFP. Redox responses of the ferrocene group in the FME or AFP on the modified electrode were observed. FME/polyamide II electrode shows the redox peaks at 0.21 and 0.30 V. AFP/polyamide II electrode shows the peaks at 0.30 and 0.22 V. The peak potentials are almost in agreement with those of the ferrocene derivatives in the aqueous solutions (for example, with FME,  $E_{pa} = 0.22$  V and  $E_{pc} = 0.20$  V). The amount of the modified ferrocene derivatives on the electrode was estimated from the peak area of the voltammograms. In this case the amount of ferrocene is electron

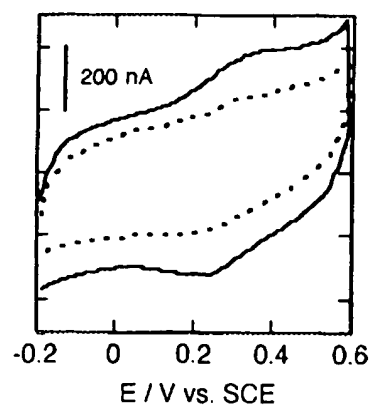


FIG. 4. Cyclic voltammograms for FME/polyamide II electrode (dotted line) and AFP/polyamide II electrode (solid line) in pH 6 buffer solution. Scan rate 20 mV s<sup>-1</sup>.

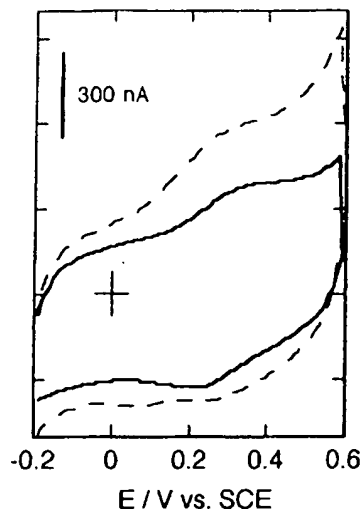


FIG. 5. Cyclic voltammograms for AFP/polyamide I electrode (dotted line) and AFP/polyamide II electrode (solid line) in pH 6 buffer solution. Scan rate  $20 \text{ mV s}^{-1}$ .

through path did not accounted in this measurement. On the FME/polyamide II electrode, the amount of FME was  $3.9 \times 10^{-14} \text{ mol cm}^{-2}$ . On the AFP/polyamide II electrode, the amount of AFP was  $1.8 \times 10^{-13} \text{ mol cm}^{-2}$ . The value of AFP/polyamide II between AFP and polyamide II is more effective than that between FME and polyamide II. It is probably due to the number of hydrogen bonding sites per ferrocene derivative. FME has a hydroxyl group that is interactive with the amide group in the polymer. AFP has an amino group and a carboxyl group which are interactive sites.

Anodic scan response of adsorbed AFP on the polyamide I modified electrode was similar to that of adsorbed AFP on the polyamide II electrode. The amount of the adsorbed AFP was  $1.492 \times 10^{-13} \text{ mol cm}^{-2}$  on the polyamide I modified electrode and  $1.803 \times 10^{-13} \text{ mol cm}^{-2}$  on the polyamide II modified electrode. AFP/polyamide II electrode showed one cathodic peak at 0.22 V. However, in the cathodic scan of polyamide I electrode, two cathodic peaks, at 0.056 and 0.252 V, were observed. Some differences were observed on the cathodic responses of the ferrocene derivatives on the modified electrode. It suggests that the interaction between oxidized AFP and normal AFP occurred. The distance among ferrocene rings on the polyamide I modified surface is smaller than that on the polyamide II modified electrode. The adsorption state of the ferrocene derivatives on the polyamide modified electrode is dependent on the created surface structure of adsorbed polyamide, namely, concerning methylene chain length in the polymer main chain.

## ACKNOWLEDGMENT

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# Extended-Chain Polyamides: Polyoxamides and Polyfumaramides

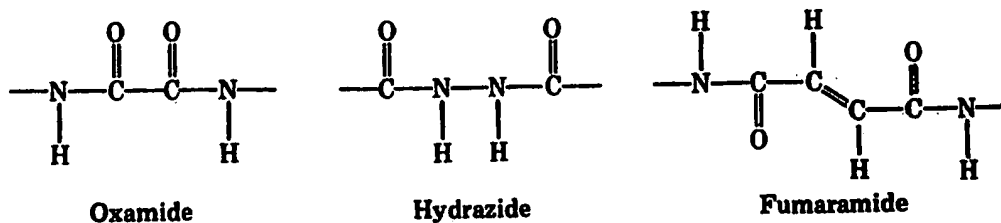
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## Synopsis

The synthesis of polyamides from short-chain aliphatic diacids, such as oxalic and fumaric acids, is difficult because of the thermal instability and volatility of the intermediates and side reactions with the polymerization media. A variety of synthetic routes to these polymers has been explored. Several aromatic polyoxamides with high molecular weight were obtained in high yield by an acid chloride vapor-solvent-water interfacial process. Polyoxamides of intermediate molecular weight also were obtained by preparation of oligomers from diamines and oxalic diesters and condensing these oligomers further in a thermal polymerization step. Aromatic polyfumaramides and terephthalamidefumaramides were prepared by modified solution procedures in amide solvents. Another route to polyfumaramides was the synthesis of *N,N'*-bis(4-aminophenyl)fumaramide and its use as a diamine with diacid chloride. The 1,4-phenylene and benzidine polyfumaramides and oxamides have extended-chain structures in solution in sulfuric, chlorosulfonic, and fluorosulfonic acids. Some of the polymers were soluble enough to yield liquid crystalline solutions. High-tenacity high-modulus fibers from poly(1,4-phenylene fumaramide/terephthalamide)s are described.

## INTRODUCTION

As a continuation of research on stiff-chain polyamides, we wished to determine if oxamide and fumaramide units would provide the extended-chain structure in polymer solutions needed to achieve the liquid crystalline state. Accomplishment of this objective has been disclosed in previous publications.<sup>1-3</sup> In other articles and patents the formation of liquid crystalline solutions from aromatic polyhydrazides has been described.<sup>4-6</sup> The oxamide unit is structurally isomeric with a hydrazide unit, but the inversion of the amide groups causes major changes in polymer solubility, thermal stability, and other characteristics.



The purpose here is to describe in greater detail the synthesis of aromatic polyoxamides and fumaramides and the conditions under which liquid crystalline solutions are obtained.

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## BACKGROUND

Polyoxamides have higher melting points than analogous polyamides from longer-chain aliphatic diacids. 6-2 Polyamide, for example, melts at 315–320°C with some decomposition.<sup>7,8</sup> Many articles and patents report encounters with thermal instability during the preparation or processing of polyoxamides, especially at temperatures above about 250°C. The severity of the decomposition is dependent on many other factors such as chemical structure, molecular weight, exposure time, the atmosphere, moisture, residual and adventitious catalysts. Shalaby et al.<sup>7</sup> have concluded from the thermal gravimetric analysis under nitrogen of several pure high-molecular-weight aliphatic polyoxamides that these polymers are comparable in thermal stability to conventional polyamides such as 6-6, 6, and 12. Limited thermal stability is not a deterrent for many uses, and the polyoxamides are reported to have other valuable attributes such as stability to ultraviolet light, low water absorption, and increased tensile modulus.

The lack of thermal stability, however, has been a major problem in obtaining high-molecular-weight polymers. Many routes to synthesis have been employed with only limited to moderate success. Some procedures which have given quite high molecular weights have been short on yield. Synthesis of high-molecular-weight polymers by the melt polycondensation route of Carothers from a diamine oxalate is prevented by thermal decomposition of the oxalic acid, as well as decomposition of the polymer in many cases.

A much used synthetic route has been the reaction of a diester of oxalic acid with a diamine.<sup>7,9,12</sup> A variety of catalysts have been used in this process.<sup>7,10-12</sup> A two-stage procedure of forming a prepolymer at low temperature and then postpolymerizing as a melt or in a solid state has yielded high-molecular-weight aliphatic polyoxamides.<sup>7,9-13</sup>

Various means have been tried for lowering the reaction temperature and thus avoiding thermal decomposition such as the use of diluents, solid-state and suspension reactions, and modification of the polymer structure for lower melting point. For example, Oldham<sup>13</sup> recommends ethylene glycol as an effective medium for the reaction of aliphatic diamines and dibutyl oxalate at 150–170°C.

Vogl and Knight<sup>8</sup> have studied the preparation of polyoxamides by ring opening of cyclic oxamides. Their melt process yielded polymers with inherent viscosities of 0.3–0.5. In spite of high reaction rates, slow thermal decomposition was observed.

Standard interfacial polycondensation has not been useful because of rapid hydrolysis of the diacid chloride. In low-temperature-solution polycondensations other side reactions are encountered. Fedotova and Zakoshchikov<sup>14</sup> have reported a two-stage process which yielded the polyoxamide from 3,3'-dimethyl-4,4'-diaminodiphenylmethane with a maximum  $\eta_{sp}$  of 1.17 (0.5% conc.) and a yield of ca. 60%. The diamine and diacid chloride were combined in methylene chloride to form an oligomer and this was allowed to react with equivalent aqueous alkali.

Hall and Berge<sup>15</sup> prepared the aromatic polyoxamide of 2,2-bis(4-amino-phenyl)propane from the diamine and diphenyl thioloalate in tetramethylene cyclic sulfone at 160°C. The initial polymer, obtained in 100% yield, had an inherent viscosity of 0.40. After the polymer was heated 18 hr under vacuum at 250°C, the inherent viscosity was 0.60.



In 1960 Sokolov and his co-workers<sup>16-18</sup> introduced a new gas-liquid process which yielded good molecular weight ranges for polyoxamides from a variety of diamines but the polymer yields were about 60% at best. The process employs an aqueous solution of the diamine and oxalyl chloride vapor in an inert gaseous diluent. In the course of their extensive studies they prepared the polyoxamides from hexamethylenediamine, 1,4-phenylenediamine, and benzidine with intrinsic viscosity/percent yield as follows: 1.1/58, 1.44/66, 1.62/56. Sokolov and Astakhova<sup>19</sup> examined the use of inert organic liquids as the solvent for hexamethylenediamine in the gas-liquid process, but obtained lower intrinsic viscosities and yield than when water was used.

In addition to the research on homopolyoxamides and random copolymers, there have been a number of studies on alternating amide-oxamides. The general approach has been to preform a diamine having a central oxamide unit substituted by two aminoarylene or aminoalkylene groups. This intermediate can then be used in appropriate interfacial or solution systems with diacid chlorides to produce high polymers. A recent article by Chang and Vogl<sup>20</sup> describes aliphatic amide-oxamides and Dobinson and Silver<sup>21</sup> have prepared wholly aromatic polyamide-oxamides.

Polyfumaramides and substituted fumaramides have been prepared from a variety of aliphatic diamines and piperazines by Mortillaro and co-workers,<sup>22</sup> using the diacid chlorides and interfacial polycondensation. Many of the polymers had high molecular weights. None were fusible. Kolesnikov and Maloshitskii<sup>23</sup> prepared low-molecular-weight polyfumaramides from phenylene diamines and benzidines by interfacial polycondensation. Fedotova and co-workers<sup>24</sup> obtained higher molecular weights with *N*-substituted aromatic diamines. These *N*-substituted polyamides were soluble in benzene and were meltable.

## RESULTS AND DISCUSSION

A basic requirement for most polymer characterization studies is that one must be able to prepare the materials in suitably high molecular weight. Therefore a major portion of this study was devoted to polymer synthesis. The principal objective was to prepare and evaluate polyoxamides and polyfumaramides from diamines having chain-extending bonds which were coaxial or parallel and oppositely directed.

### Polyoxamide Synthesis

Although the synthesis of polyoxamides from active oxalyl esters has been widely applied for aliphatic polyoxamides, to our knowledge the process has not been applied to aromatic polyoxamides, except for the work of Hall and Berge.<sup>15</sup> They used phenyl thioloalate with several aromatic diamines.

### Aminolysis of Phenyl Thioloalate

The procedure of Hall and Berge was tried with 1,4-phenylenediamine and produced the polymer with an inherent viscosity of 0.5 dl/g in 97% yield without heat treatment afterward.

### Oligomers by Aminolysis of Other Oxalate Esters

The general procedures of Stamatoff<sup>10,11</sup> and Bruck<sup>12</sup> were applied to 1,4-phenylenediamine. Some of the variables examined are:

*Esters:* Methyl, butyl, phenyl

*Solvents:* Diphenyl ether, cyclic tetramethylene sulfone, *o*-dichlorobenzene, toluene

*Catalysts:*  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{Mn}(\text{H}_2\text{PO}_2)$ , imidazole, tetraisopropyl titanate

*Catalyst amount:* 7–15 ppm

*Temperature:* 27°C to reflux temperature

*Time:* 2–16 hr

The oligomers precipitated from all of the solvents during the reaction and were isolated by filtration and washing with solvents. The maximum inherent viscosities were 0.08 for methyl ester, 0.10 for butyl ester, and 0.26 for phenyl ester. The oligomers from the phenyl ester were used in the thermal polymerizations discussed in the following section, although the lower oligomers gave a similar degree of response to heating.

### Thermal Polymerization of Oligomers

Oligomer samples from aminolysis of phenyl oxalate ( $\eta_{\text{inh}}$  0.24–0.26) were subjected to heating as suspensions in diphenyl sulfone with stirring under nitrogen (Figs. 1 and 2). The catalysts ( $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ , and tetraisopropyl titanate) were incorporated during oligomer preparation. At 250°C each of the three samples gives a maximum inherent viscosity after 1.5 hr of heating. Thereafter, the effect of degradation exceeds that of polymer growth, although the sample catalyzed by arsenous oxide decreased very little in inherent viscosity. Varying

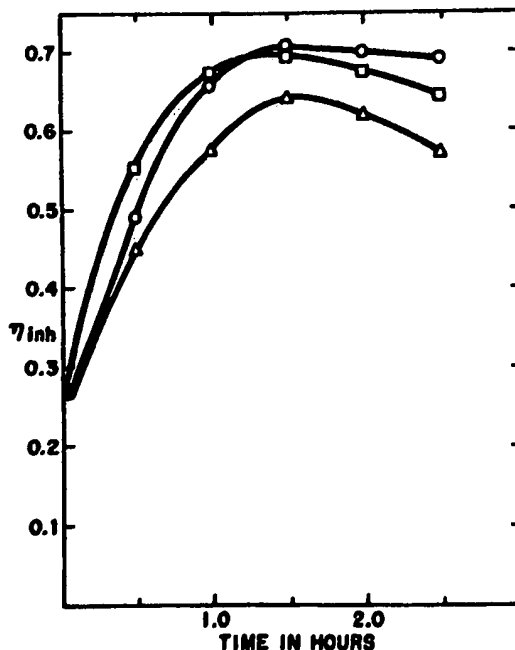


Fig. 1. Inherent viscosity versus time at 250°C for polymerization of poly(1,4-phenylene oxamide) oligomer in diphenyl sulfone with several catalysts: (O)  $\text{As}_2\text{O}_3$ , (□) tetraisopropyl titanate, (Δ)  $\text{Sb}_2\text{O}_3$ .

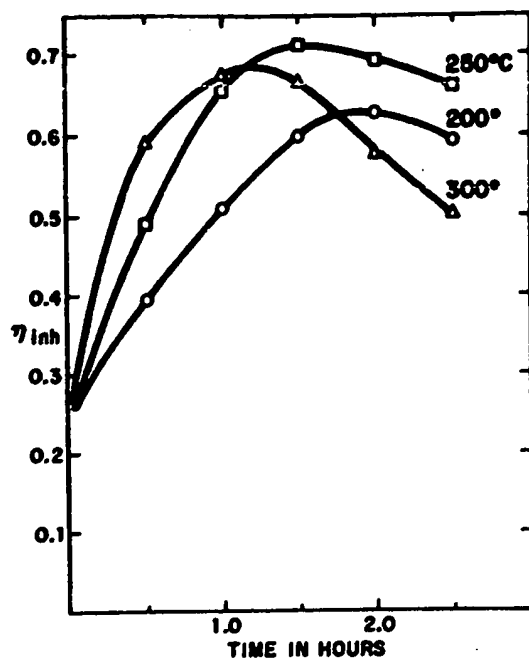


Fig. 2. Inherent viscosity versus time at 200, 250, and 300°C for polymerization of poly(1,4-phenylene oxamide) oligomer in diphenyl sulfone with  $As_2O_3$  catalyst.

the temperature from 200 to 300°C for the oligomer containing arsenous oxide (Fig. 2) gave more rapid polymerization as the temperature was raised but the maximum degree of polymerization ( $\eta_{inh}$  0.72) was attained at 250°C.

A related series of polymerizations was carried out on powdered oligomer samples heated in polymer tubes under reduced pressure (0.67 kPa) for varying times and temperatures (Figs. 3 and 4). Results similar to the suspension polymerizations were obtained with the arsenous oxide sample giving a maximum

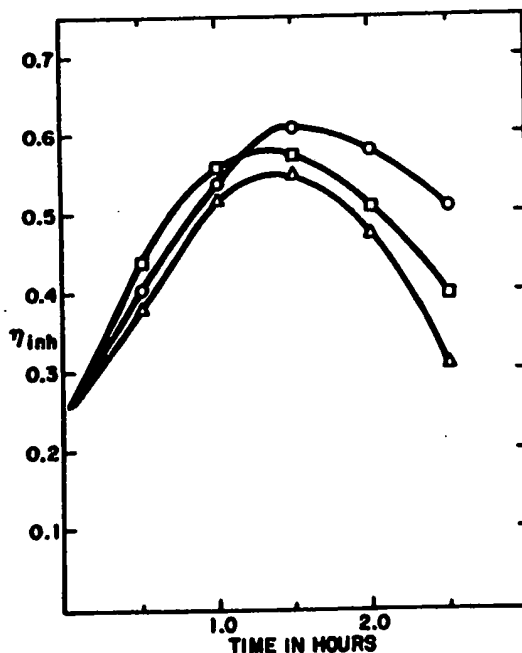


Fig. 3. Inherent viscosity versus time at 250°C for polymerization of poly(1,4-phenylene oxamide) oligomer as a powder with several catalysts: (O)  $As_2O_3$ , (□) tetraisopropyl titanate, (Δ)  $Sb_2O_3$ .

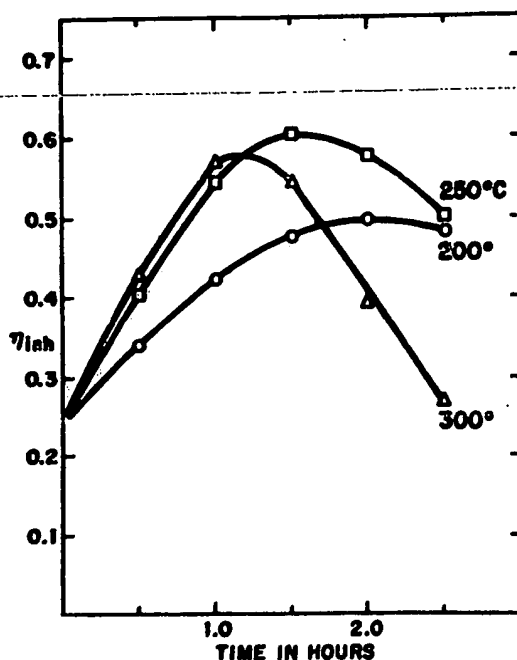


Fig. 4. Inherent viscosity versus time at 200, 250, and 300°C for polymerization of poly(1,4-phenylene oxamide) oligomer as a powder with  $As_2O_3$  catalyst.

inherent viscosity of 0.61 in ca. 1.5 hr at 250°C. The solid-state polymerization gave a more rapid degradation rate than suspension polymerization. This is shown by the lower peaks in the viscosity-time curves and the greater fall in viscosity with time for nearly all samples.

#### Oxalyl Chloride Vapor-Solvent-Water Polymerization Method

As indicated in the Introduction, Sokolov has explored the preparation of polyoxamides from aqueous diamine solutions and oxalyl chloride vapor diluted with nitrogen. He has determined the effect of many variables on molecular weight and yield. High-molecular-weight polymers were obtained from both aliphatic and aromatic diamines. The principal shortcoming of the process is the rather low yields of polymer (up to ca. 65% based on diamine).

We have found that much higher yields of polymer result when both water and a water-immiscible organic solvent are used and polymers with high viscosities can be obtained. The addition of a third phase greatly increases the complexity of the system. Several variables have been studied in a limited way with 2,2'-dimethyl-4,4'-diaminobiphenyl as the diamine.

The reactions were carried out in a small resin kettle equipped with a 2000-rpm disk stirrer. Equal volumes of water and organic solvent phases were used with the diamine and any alkali dissolved in the mixed phases. Oxalyl chloride at 5–20 mole % excess (based on diamine) was warmed in a generator and carried by means of a flow of dry nitrogen such that a gas mixture of 25% by volume of acid chloride passed over the surface of the stirred liquids at a rate of 2 liter/min.

Preparation of poly(2,2'-dimethyl-4,4'-biphenylene oxamide) (DMePP-2) was first carried out in chloroform-water at 55°C and a diamine concentration of 0.025M and with varying amounts of sodium hydroxide (Fig. 5). The inherent

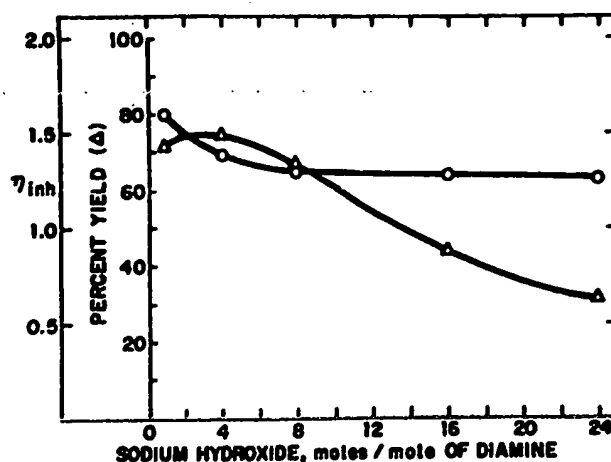


Fig. 5. Effect of sodium hydroxide concentration on inherent viscosity and yield of poly(2,2'-dimethyl-4,4'-biphenylene oxamide) prepared in an oxalyl chloride vapor-chloroform-water system. Diamine, 0.025*M* in total liquid phase; temperature, 55°C.

viscosity and yield increased as the amount of alkali decreased. Therefore, additional experiments were conducted in which the diamine concentration was varied and aqueous sodium hydroxide was added at a rate to keep the pH between 6.8 and 7.2 (Fig. 6). The result was an increase in yield throughout the concentration range and a marked increase in inherent viscosity of the DMePP-2 at low diamine concentrations (from 1.6 to 2.2). Figure 7 shows similar polymerizations with bis(4-aminophenyl)methane and 1,4-phenylenediamine in methylene chloride-water at 35°C. Both inherent viscosity and the yield of the products improve with dilution of the polymerization system. The curves indicate that some gain in inherent viscosity might be attained by further dilution, but a drop in product viscosity should be encountered in this range as well.

The effect of temperature on the polymerization of DMePP-2 was determined in methylene chloride, chloroform and chlorobenzene under the optimum conditions developed for chloroform (Fig. 8). In each case the degree of polymerization increased as the temperature increased. This effect has been interpreted

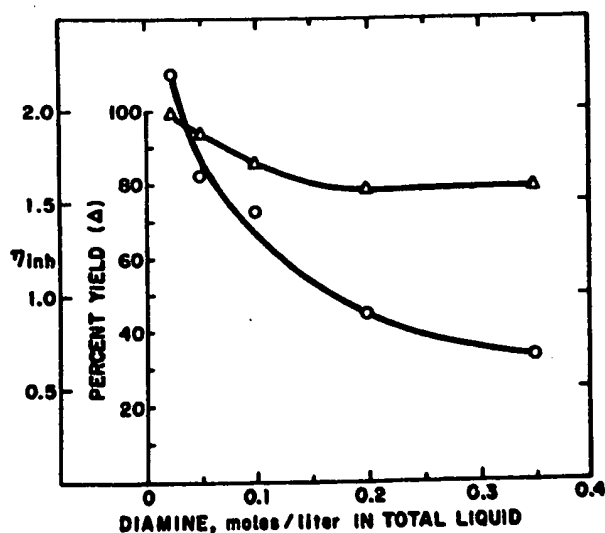


Fig. 6. Inherent viscosity and yield versus diamine concentration for the preparation of poly(2,2'-dimethyl-4,4'-biphenylene oxamide) in an oxalyl chloride vapor-chloroform-water system. Temperature, 55°C; pH held between 6.8 and 7.2 by automatic titration.

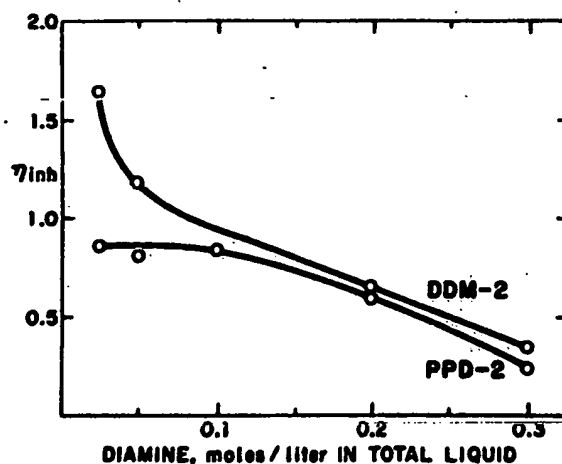


Fig. 7. Inherent viscosity versus diamine concentration for preparation of polyoxamides from 1,4-phenylenediamine and bis(4-aminophenyl)methane in an oxalyl chloride vapor-methylene chloride-water system. Temperature, 35°C; pH held between 6.8 and 7.2 by automatic titration. Yields with decreasing concentration: DDM-2, 87-98%; PPD-2, 85-95%.

in relation to the work of Sokolov as due to the lowered solubility of oxalyl chloride vapor in water and consequent reduction of hydrolysis. Chloroform-water was the superior polymerization medium. This may result from a greater swelling of the polymer or from some other favorable circumstance such as diamine partition in the phases, solvent-water ratio, or solubility of oxalyl chloride in the solvent. Obviously, there are many variables remaining to be explored. The range of polymer yields for the three solvents with increasing temperature was 88-95% (methylene chloride), 92-98% (chloroform), and 95-99% (chlorobenzene).

For comparison with the vapor-solvent-water results, DMePP-2 was prepared by standard interfacial condensation at ca. 27°C in chloroform water and with equivalents of diamine and oxalyl chloride in the same concentration range as given for Figure 6. Inherent viscosity varied only from 0.2 to 0.4 and the yield from 8 to 15%.

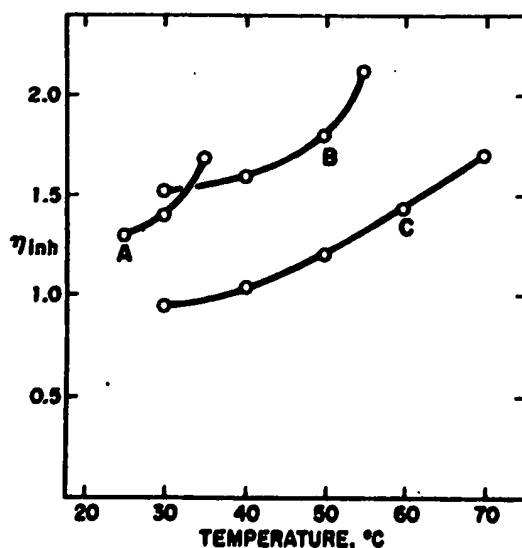


Fig. 8. Effect of temperature and solvent on inherent viscosity of poly(2,2'-dimethyl-4,4'-biphenylene oxamide) produced in an oxalyl chloride vapor-solvent-water system. Diamine, 0.025M in total liquid volume; pH held between 6.8 and 7.2 by automatic titration.

Table I presents the inherent viscosity and yield of DMePP-2 prepared under the optimum conditions found together with the results for single syntheses of a number of other polyoxamides prepared under the same conditions. Yields are all above 92%. Inherent viscosities range from 0.30 to 1.64. The low value probably results from use of low-purity diamine. Most of the others could no doubt be raised some by further experimentation.

#### Polyfumaramides by Solution Polymerization

Aromatic polyfumaramides may be prepared from the acid chlorides and diamines in alkyl-substituted amide solvents as for other aromatic-aliphatic polyamides.<sup>1,25</sup> In all such preparations there is a competing side reaction between the solvent and acid chloride. This is particularly noticeable with short-chain aliphatic diacid chlorides. The side reaction produces chain termination in the form of dialkyl amide and monoacyl amide groups. The amount of side reaction can be reduced by selecting solvents with low reactivity, such as hexamethylphosphoramide, by lowering the reaction temperature, and by diluting the diacid chloride with an inert solvent. Tables II and III report preparations in which tetrahydrofuran was used as a diluent for fumaryl and methylfumaryl chlorides with gains in the inherent viscosity of the polymer thus produced. In preparing copolymers from two diacid chlorides, one of which is especially reactive with the solvent, such as terephthaloyl chloride and fumaryl chloride, the more reactive fumaryl chloride should be introduced first while the diamine concentration is high.

Another route to reducing the effect of the side reaction is to prepare an amine-terminated diamide of the reactive intermediate. In this way the required amount of diacid chloride for the polymerization is cut in half. The first three preparations of Table II show the preparation of poly(1,4-phenylene fumaramide): (1) from *N,N'*-bis(4-aminophenyl)fumaramide,  $\eta_{inh}$  2.28; (2) from 1,4-phenylenediamine and fumaryl chloride diluted with tetrahydrofuran,  $\eta_{inh}$  1.20; and (3) from 1,4-phenylenediamine and undiluted fumaryl chloride,  $\eta_{inh}$  0.77.

The marked rise in inherent viscosity of the fumaramide/terephthalamide series (Tables II and III) with increasing terephthalamide content may reflect both a reduction in side reaction with the solvent and greater purity of the

TABLE I  
Polyoxamides Prepared by Gas-Liquid Interfacial Polycondensation<sup>a</sup>

Diamine	Inherent viscosity (dl/g)	Yield <sup>b</sup> (%)
2,2'-Dimethyl-4,4'-diaminobiphenyl	2.20	99
Bis(4-aminophenyl)methane	1.64	97
1,4-Phenylenediamine	0.87	92
Chloro-1,4-phenylenediamine	0.97	92
<i>trans</i> -1,4-Cyclohexylenediamine	0.76	92
1,5-Diaminonaphthalene	0.30	~95

<sup>a</sup> Polymerization in  $\text{CHCl}_3\text{-H}_2\text{O}$  (1/1 v/v) with diamine at 0.025*M* in the total volume, a temperature of 55°C, and pH 6.8-7.2.

<sup>b</sup> Based on diamine.

TABLE II  
Poly(1,4-Phenylene Fumaramide/Terephthalamide)s by a Solution Process

Fumaramide/ terephthalamide (mole ratio)	Procedure <sup>a</sup>	Scale of preparation (moles)	Yield (%)	Inherent viscosity (dl/g)
100/0	A	0.01	100	2.28
100/0	B	0.03	98	1.20
100/0	C	0.03	98	0.77
95/5	B	0.03	98	1.05
90/10	B	0.03	100	1.10
80/20	B	0.03	100	1.05
60/40	D	0.30	100	1.91
40/60	D	0.30	100	3.67
30/70	D	0.30	100	3.41
20/80	D	0.30	100	4.61
10/90	D	0.30	100	6.16

<sup>a</sup> See Experimental section for details of procedure. A: HMPA/NMP (30 ml/30 ml) and *N,N'*-bis(4-aminophenyl)fumaramide as the diamine. B: HMPA/NMP (43 ml/87 ml) with fumaryl chloride added as a solution in 15 ml of tetrahydrofuran, followed by solid terephthaloyl chloride if used. C: Like B without tetrahydrofuran. D: HMPA/NMP (650 ml/650 ml) with undiluted fumaryl chloride.

terephthaloyl chloride. Whether there is also a difference in the viscosity-molecular weight relationship is not known.

### Optically Anisotropic Solutions

Polyoxamides and polyfumaramides derived from diamines which have their chain-extending bonds coaxial or parallel and oppositely directed formed liquid crystalline solutions in sulfuric and sulfonic acids when their molecular weights were sufficiently high and solubility was high enough to exceed the critical concentration. Some of the solution tests are summarized in Tables IV and V.

The acids employed were 96–100% sulfuric acid, chlorosulfonic acid, and fluorosulfonic acid. In many instances solubility was increased by raising the temperature and thereby forming a liquid crystalline solution. On the other

TABLE III  
Poly(1,4-Phenylene Methylfumaramide/Terephthalamide)s Prepared by a Solution Process

Methylfumaramide/ terephthalamide (mole ratio)	Procedure <sup>a</sup>	Yield (%)	Inherent viscosity (dl/g)
100/0	A	100	1.22
100/0	B	97	0.69
80/20	C	90	0.56
50/50	C	100	1.15
20/80	C	100	2.55
5/95	C	95	4.76

<sup>a</sup> See Experimental section for a detailed procedure; 0.03 mole preparations. A: Dimethylacetamide (52 ml) at 27°C with methylfumaryl chloride added as a solution in 10-ml tetrahydrofuran. B: HMPA/NMP (17 ml/35 ml) with undiluted methylfumaryl chloride added dropwise over 60 min at 25°C. C: HMPA/NMP (43 ml/87 ml) as in B, followed by solid terephthaloyl chloride.



TABLE IV  
Preparation of Solutions from Polyoxamides

Polymer from <sup>a</sup>	$\eta_{inh}$ (dl/g)	Polymer solution			Solution state at rest
		Solvent	Solids (%)	Temp. (°C)	
DMePP	1.55	FSO <sub>3</sub> H	15-20	>50	Anisotropic
	1.34	ClSO <sub>3</sub> H	20	>50	Isotropic
			25	>50	Incomplete solution
		100.3% H <sub>2</sub> SO <sub>4</sub>	8	27	Isotropic
			20	Up to 100	Paste
DDM	1.64	100% H <sub>2</sub> SO <sub>4</sub>	20	27	Isotropic
PPD	0.9	100% H <sub>2</sub> SO <sub>4</sub>	15-20	50	Insoluble
CIPPD	0.67	ClSO <sub>3</sub> H	15-20	50	Anisotropic
HPPD	0.76	100% H <sub>2</sub> SO <sub>4</sub>	15-20	Up to 100	Insoluble
DAN	0.3	100% H <sub>2</sub> SO <sub>4</sub>	15	Up to 100	Insoluble

<sup>a</sup> DMePP: 2,2'-dimethyl-4,4'-diaminobiphenyl; DDM: bis(4-aminophenyl)methane; PPD: 1,4-phenylenediamine; CIPPD: chloro-1,4-phenylenediamine; HPPD: *trans*-1,4-diaminocyclohexane; DAN: 1,5-diaminonaphthalene.

hand, raising the temperature of an optically anisotropic solution may cause it to become isotropic. The process is reversible.

### Fiber Preparation

High-strength high-modulus fibers were prepared from poly(1,4-phenylene fumaramide/terephthalamide)s, as shown in Table VI. Spinning was by dry-jet/wet-spinning process described by Blades.<sup>2,3</sup> Sulfuric acid was used as the

TABLE V  
Preparation of Solutions from Polyfumaramides

Fumaramide from <sup>a</sup>	$\eta_{inh}$ (dl/g)	Polymer solution			Solution state at rest
		Solvent	Solids (%)	Temp. (°C)	
PPD-Δ4	2.28	FSO <sub>3</sub> H	20	27	Isotropic
			25	>50	Isotropic
			27	>50	Anisotropic
CIPPD-Δ4	0.67	96% H <sub>2</sub> SO <sub>4</sub>	20	25	Isotropic
			27	25	Isotropic
			31	25	Anisotropic
	0.45	99.7% H <sub>2</sub> SO <sub>4</sub>	27	>50	Isotropic
			31	>50	Isotropic
PPD-Δ4/T	1.91	100.2% H <sub>2</sub> SO <sub>4</sub>	33.7	>50	Anisotropic
			20	68	Anisotropic
			20	>50	Anisotropic
	60/40	FSO <sub>3</sub> H	20	>50	Anisotropic
	40/60	100.2% H <sub>2</sub> SO <sub>4</sub>	20	80	Anisotropic
PPD-MeΔ4	20/80	FSO <sub>3</sub> H	20	>50	Anisotropic
	2.75	100% H <sub>2</sub> SO <sub>4</sub>	20	27	Isotropic
	1.22	100% H <sub>2</sub> SO <sub>4</sub>	25	>80	Anisotropic
PPD-MeΔ4/T	50/50	100% H <sub>2</sub> SO <sub>4</sub>	20	27	Anisotropic
	20/80	100% H <sub>2</sub> SO <sub>4</sub>	20	27	Anisotropic

<sup>a</sup> Δ4 and MeΔ4 represent fumaryl and methylfumaryl units; PPD: 1,4-phenylenediamine; CIPPD: chloro-1,4-phenylenediamine.

TABLE VI  
Fibers Prepared from Poly(1,4-Phenylene Fumaramide/Terephthalamide)s as Anisotropic Solutions in Sulfuric Acid<sup>a</sup>

Fumaramide/ terephthalamide (mole ratio)	Polymer $\eta_{inh}$ (dl/g)	Winding speed (m/min)	Filament properties <sup>b</sup>		
			Tex	Tenacity (dN/tex)	Orientation angle (°)
30/70	3.41	203	0.73	16.6	20
40/60	3.67	303	0.56	15.6	23
60/40	1.91	213	0.48	7.3	30

<sup>a</sup> Spun from 20% (by weight) solutions in 101.3% sulfuric acid by a dry-wet spinning process with water as the coagulation bath (ref. 3).

<sup>b</sup> Tex is the weight in grams of 1000 m of fiber. dN/tex can be converted to g/denier by multiplication by 10/9.

solvent. The high strength, modulus, and molecular orientation were attained directly in the as-spun fibers without posttreatment other than washing and drying.

The third spin in Table VI was carried out with a polymer having lower inherent viscosity than in the first two examples and resulted in fiber with lower tenacity and modulus. Molecular weight data are not available to show clearly that this is a cause. Other factors related to molecular weight and chain configuration could be involved, such as bulk solution viscosity, the proportion of anisotropic phase, and variation in chain extension or persistence length with structure of the copolymers.

## EXPERIMENTAL

### Toxicity and Other Safety Hazards

Several of the materials used in this study are classed as experimental carcinogens or are closely related in structure to other substances having carcinogenic activity in man or animals. In this category are hexamethylphosphoramide, 1,5-diaminonaphthalene, and 2,2'-dimethyl-4,4'-diaminobiphenyl. Oxalyl chloride vapor is extremely irritating to the upper respiratory tract and may cause other forms of internal poisoning. Because of its volatility and high reactivity, it is especially corrosive to the skin and eyes. It is hazardous if heated to decomposition and it reacts vigorously with water and steam.

Chloro-1,4-phenylenediamine may decompose violently when heated for the purpose of distillation or sublimation.

During storage tetrahydrofuran may develop peroxides which present an explosive hazard, especially upon distillation or evaporation. Acid chlorides react slowly with tetrahydrofuran and therefore such solutions should be prepared just before use.

### Intermediates and Solvents

Diamines and diacid chlorides were purchased or synthesized by known procedures. Diamines were purified by sublimation through a layer of silica gel under vacuum or by recrystallization from an appropriate solvent. Oxalyl esters were distilled under reduced pressure of 0.13 kPa after stirring 12-16 hr with calcium hydroxide to remove any monomer. Oxalyl chloride was distilled over calcium hydride at atmospheric pressure just prior to use.

Some further details and physical constants are given in Appendix C of ref. 18.

Solvents were purchased as reagent chemicals or were purified by distillation under reduced pressure. Amide solvents were stored over molecular sieves.

### *N,N'*-Bis(4-Aminophenyl)fumaramide

To a stirred solution of *p*-nitroaniline (28.3 g, 0.21 mole), ethyldiisopropylamine (28.0 g, 0.20 mole), and acetone (500 ml) was added dropwise through an addition funnel a solution of fumaryl chloride (15.3 g, 0.10 mole) in anhydrous ethyl ether (200 ml). The reaction was permitted to continue for an additional

20 min after which the precipitated product, *N,N'*-bis(4-nitrophenyl)fumaramide, was collected by filtration, washed twice with water, twice with methanol, and once with ether. The crude product was crystallized from 500 ml of dimethylacetamide to yield 24.5 g of yellow needles which melted at 395–400°C. This material was dissolved in warm dimethylacetamide and reduced with hydrogen in the presence of 1.0 g of palladium on charcoal. After removal of the catalyst from the warm solution, the product upon cooling crystallized as long yellow needles melting at 232°C.

ANAL. Calcd for  $C_{18}H_{12}N_4O_2$ : C, 64.84%; H, 5.45%; N, 18.91%. Found: C, 64.88%; H, 5.43%; N, 18.85%.

#### Preparation of a Phenylene Oxamide Oligomer

Diphenyl oxalate (24.2 g, 0.1 mole) was added to a stirred solution, contained in a three-necked round-bottomed flask under a nitrogen atmosphere, of 1,4-phenylenediamine (10.8 g, 0.1 mole) and arsenic trioxide (0.0162 g, 0.01 mole %) in *o*-dichlorobenzene (53 g). Precipitation of the oligomer started after the reaction had proceeded 35 min. Reflux was continued with stirring for another 3.4 hr at which time the oligomer (24.6 g, 86% yield) was isolated. Filtration and drying of the oligomer were carried out under a nitrogen atmosphere. The oligomer had an inherent viscosity of 0.26 dl/g.

Many reactions of the above type were carried out. The various solvents, catalysts, and reaction times employed are summarized in the Results and Discussion section.

#### Powder Polymerization of Phenylene Oxamide Oligomer

The above oligomer (15 g) was added to a 1.0-mm thick-walled polymer tube (30 cm long, 10 cm in diameter) while in a dry box with a nitrogen atmosphere. A two-holed rubber stopper was inserted into the top of the tube permitting maintenance of a nitrogen atmosphere through a glass capillary which extended the full length of the tube into the finely ground polymer. The resulting polymer agitation also assisted by-product removal. Evacuation (0.037 kPa) of the polymer tube was achieved by a vacuum pump attached to a tube in the second hole. The evacuated polymer tube was placed into a silicone oil bath at 250°C for 1.5 hr. Poly(1,4-phenylene oxamide) with an inherent viscosity of 0.61 at a yield of 9.2 g (93%) was obtained. Figures 3 and 4 illustrate the effects of time, temperature, and catalysts in the preparation of this polymer.

#### High-Temperature Suspension Polymerization of Phenylene Oxamide Oligomer

The oligomer (15 g) was added to 150-ml of tetramethylene sulfone in a three-necked round-bottomed flask equipped with an air-driven stirrer, reflux condenser, and thermometer. The suspension was heated at 250°C with stirring for 4 hr. Isolation of the polymer by filtration was followed by washing the polymer in acetone and drying in a vacuum oven. Polymer was obtained with an inherent viscosity of 0.72 dl/g and a 92% yield.

## Gas-Liquid Phase Preparation of a Polyoxamide

The polymerization equipment consisted of three principal parts: (1) an oxalyl chloride vapor generator in the form of a 50-ml round-bottomed flask equipped with a nitrogen inlet and a heater; (2) a heated glass transfer tube (0.81 mm i.d.) extending from the generator into the reaction vessel with the outlet about 2.5 cm above the surface of the stirred liquids; and (3) the reaction vessel (a 500-ml resin kettle) equipped with an air-driven shear-disk stirrer, reflux condenser, automatic titrator, and heater.

The rate of introduction of oxalyl chloride was first calibrated by placing measured amounts of oxalyl chloride in the generator heated to 59°C, passing dry nitrogen through at varying known rates, and determining the oxalyl chloride absorbed in stirred methylene chloride in the reaction vessel. From these data conditions were chosen so that a gas mixture containing 25% by volume of oxalyl chloride could be introduced at a slow reproducible rate.

Gaseous oxalyl chloride (5.0 mole % excess) in nitrogen was introduced over a period of 15 min into the reaction vessel containing 100 ml of chloroform, 100 ml of water, and 1.03 g (0.005 mole) of 2,2'-dimethyl-4,4'-diaminobiphenyl, which was stirred at 2000 rpm and maintained at 55°C. The pH of the mixture was maintained at between 6.8 and 7.2 by aqueous sodium hydroxide added through the automatic titrator. During the initial stage of the reaction a thin film of polymer coated all the surfaces, but as the reaction continued the polymer and liquids formed a thick slurry. The reaction mixture was diluted with water. The product was collected by filtration and washed twice with water and once with methanol with the aid of a blender. The polymer, dried under vacuum at 80°C, was obtained in 98% yield and had an inherent viscosity of 2.20 dl/g.

## Poly(1,4-Phenylene Fumaramide)

To a stirred solution of 1,4-phenylenediamine (3.24 g, 0.03 mole) in a dry-ice-cooled (-10°C) mixture of hexamethylphosphoramide/*N*-methylpyrrolidone (43 ml/87 ml) was added dropwise an ice-cooled solution of fumaryl chloride (4.63 g, 0.0303 mole) in 15 ml of tetrahydrofuran. The cooling bath was removed after 10 min and the combined stirred ingredients were allowed to warm to room temperature for the next 50 min, after which lithium carbonate (1.43 g, 0.02 mole) was added. The reaction mixture was stirred an additional 3 hr at room temperature and then combined with water to precipitate the polymer which was collected, washed separately with water and with methanol, and dried in a vacuum oven at 80°C. The dried polymer had an inherent viscosity of 1.20 dl/g. When the preparation was done without the tetrahydrofuran, the product inherent viscosity was 0.77 dl/g. The yields of polymer were essentially quantitative.

## Poly(1,4-Phenylene Fumaramide) from Preformed Diamide

To a stirred solution of *N,N'*-bis(4-aminophenyl)fumaramide (2.83 g, 0.01 mole) in hexamethylphosphoramide/*N*-methylpyrrolidone (30 ml/30 ml), cooled as in the preceding preparation, was added dropwise undiluted fumaryl chloride (1.53 g, 0.01 mole). After 35 min of stirring a thick gel resulted. The gel was combined with water in a blender to precipitate the polymer, which was collected,

washed twice with water, twice with methanol, and dried under vacuum at 100°C. The polymer had an inherent viscosity of 2.28 dl/g.

*Poly(1,4-Phenylene Methylfumaramide)*

Methylfumaryl chloride (5.03 g, 0.03 mole) in tetrahydrofuran (10 ml) at room temperature was added over a 60-min period through a dropping funnel to a solution of 1,4-phenylenediamine (3.24 g, 0.03 mole) in dimethylacetamide (52 ml). The reaction was carried out in a 250-ml round bottomed flask equipped with a nitrogen inlet, calcium chloride drying tube, and an air-driven glass stirrer. Rapid stirring of the nitrogen-blanketed system was continued for 3 hr after mesaconyl chloride addition. The pastelike system was poured into water and the precipitated polymer was filtered and washed, two times with water and once with methanol, in a blender. The polymer, dried in a vacuum oven at 80°C had an inherent viscosity of 1.22 dl/g (6.1 g, 100% yield). When the same reaction was carried out in hexamethylphosphoramide (17 ml) and *N*-methylpyrrolidone (35 ml) as the polymerization solvent, an inherent viscosity of 0.69 dl/g resulted (5.9 g, 97% yield).

*Poly(1,4-Phenylene Fumaramide/Terephthalamide) (10/90)*

1,4-Phenylenediamine (32.4 g, 0.3 mole) was added to a stirred mixture of hexamethylphosphoramide/*N*-methyl-2-pyrrolidone (650 ml/650 ml). The solution was cooled to -10°C in a dry-ice/acetone bath. After this cooling bath was removed and replaced with an ice-water bath, fumaryl chloride (4.59 g, 0.03 mole) was added to the stirred solution. After 2 min, terephthaloyl chloride (54.81 g, 0.27 mole) was added slowly to the stirred reaction mixture. Stirring was continued for a total of 2 hr 40 min, with the reaction vessel being cooled externally for 1 hr 40 min. The reaction mixture was permitted to stand at ambient temperature for two days, after which it was combined with water to precipitate the copolymer which was collected, washed separately with water and methanol, and dried *in vacuo* overnight at 80°C. The dried polymer had an inherent viscosity of 6.16.

*Dilute Solution Viscosity*

Inherent viscosities [ $\eta_{inh} = (2.3 \log \eta_{rel})/c$ ] were determined in 96-98% sulfuric acid at 30°C and a concentration (*c*) of 0.5 g/100 ml of solution. The values are in deciliters per gram.

*Fiber Tensile Properties*

Filament properties were measured on fibers which had been conditioned at 21°C and 65% relative humidity for at least 16 hr. The breaking tenacity (*T*), breaking elongation (*E*), and the initial modulus (*M<sub>i</sub>*) were obtained by breaking single filaments at a gage length (distance between clamping jaws) of 2.54 cm on an Instron tester (Instron Engineering Corp., Canton, MA). Samples were elongated at a constant rate of extension (10% extension/min for fibers with *E* under 8 and 60% extension/min for *E* of 8% or above). The tex of a filament

(weight/1000 m) was calculated from its functional resonant frequency, determined by vibrating a 7-9-cm length of fiber under tension with changing frequency (ASTM method D1577-66, part 25, 1968). This filament is then used for one break. Three or more samples are broken and the results averaged.

### Fiber Orientation Angle

Wide-angle x-ray diffraction patterns were obtained with a Warhus pinhole camera and Phillips x-ray generating unit No. 12045 having a copper fine-focus diffraction tube and a Ni  $\beta$  filter. The distance from the parallel bundle of fibers was 50 mm. The arc length in degrees between the half-maximum intensity points of a principal equatorial diffraction spot is reported as the orientation angle of the sample.<sup>23</sup>

### Recognition of the Liquid Crystalline Solutions

The liquid crystalline state in solutions is recognized by an opalescent appearance, especially under shear, depolarization of plane polarized light, a critical concentration point at which there is a marked decrease in bulk solution viscosity with increasing concentration, and magnetic field effects.<sup>1,27-29</sup>

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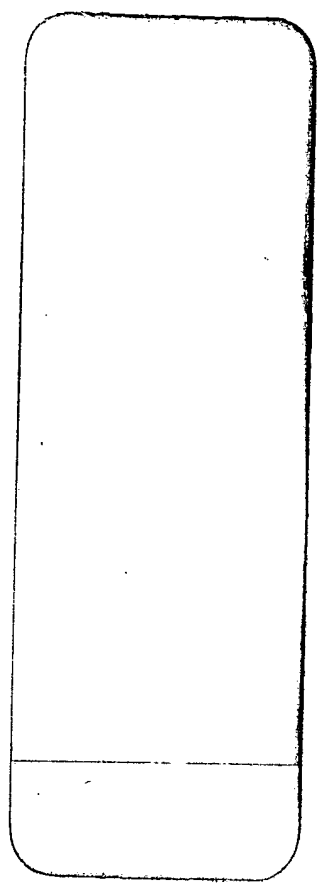
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